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DYNAMIC RELATIONS BETWEEN PLANT AND SOIL, WITH SPECIAL REFERENCE TO THE SUPPLY OF WATER AND OXYGEN

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From the viewpoint of plant physiology it is advantageous to consider the living plant and its environment as the two members of a system in which the environment operates to supply material and energy to the organism and to dispose of material and energy that pass out of the organism, while the organism itself acts in a reciprocating manner, allowing material and energy to enter from the surroundings or to pass out into the surroundings. To understand the relations between organism and environment it is essential that we should be able to measure and describe, with adequate degree of precision, the influential environmental conditions and their fluctuations, as well as the plant responses that are related to these influences. The environmental system needs to be described in terms of its capacity to supply essential things to the plant and in terms of its ability to remove substances and energy that may be given off by the plant.

That many kinds of soil conditions influence the activities of plants has long been appreciated in a general way but it is only recently that we have been in a position to begin to study some of these conditions by means of methods that promise to give direct measures of the capacity of the soil to influence the plant. The soil system is to be regarded as a machine capable of delivering substances and energy to the organism at rates that may be either adequate or inadequate for good growth, or for a certain type of growth, etc. If the power of the soil system to deliver some necessary thing is inadequate the system limits the physiological processes correspondingly; but if the supplying power of the soil is adequate with respect to the essential in question, then, of course, that particular supplying power is not a limiting condition. If, in this second case, we wish to improve growth for a given plant one or more of the other environmental influences must be modified.

The only soil conditions thus far directly measured as supplying powers are those of moisture and of oxygen and only the water-supplying power of the soil has as yet been studied in the field. A general method is available for the study of the capacity of the soil to supply carbon dioxide, but this has not yet been applied. Temperature measurement will perhaps meet our needs with reference to the soil's capacity to supply heat to plant roots, at least for a long time; for the heat interchange between plant and soil is not complicated, as is that between plant and air, by radiation and environmental flow (wind). Methods for studying the capacities of the soil to supply ions, salts and other substances excepting water, oxygen and carbon dioxide, remain yet to be devised. With these three exceptions we are still confined to static measurements, measurements of amounts of the given substances in a volume or weight unit of soil.

The purpose of this little paper is to summarize, in the form of a simple statement, the results of many years of research, in which a large number of students and assistants, at the Laboratory of Plant Physiology of the Johns Hopkins University and at the Desert Laboratory of the Carnegie Institution of Washington, have taken part. This statement presents critical values of the water-supplying power and the oxygen-supplying power of the soil, values that approximately represent the minima for good growth and health in ordinary plants. So far as I am aware, no similar statement with regard to dynamic soil conditions has hitherto been attempted by any one and the statement here made for the first time may serve as a concrete illustration of significant progress in the study of environmental process rates as these may influence plant life. Similar progress has been made in the study of conditions of moisture and radiation in the aerial environment of plants, but with that portion of the environment we shall not be concerned in the present publication. It is desirable that other dynamic characteristics of plant surroundings may become measurable in the near future and that the point of view here illustrated may eventually become common in physiological and ecological discussion.

We now have a fairly satisfactory method for measuring the water-supplying power of the soil about the roots of a plant.[2] For the climatic conditions of a Baltimore summer such plants as white clover and Kentucky blue-grass on lawns continue to appear healthy as long as the adjacent soil is capable of supplying water to a water-absorbing surface, with which it is in capillary contact, at a rate not lower than about 8 mg. per hour per square centimeter of surface, or 80 g. per hour per square meter. When this capacity rate falls to one-half of the value just given these plants become vegetatively dead within 2 or 3 days and the lawn then appears tawny instead of green. For a study of this dynamic feature

of the soil it is not primarily necessary to have any information about either the kind of soil or its water content. Shortly after a heavy rain, when superficial run off and subterranean drainage have ceased, the water-supplying power of the wet region of the soil may correspond to a rate of delivery one hundred times as great as the critical one just mentioned.

The capacity of a soil to supply oxygen to roots can also be measured directly now,[3] although the necessary apparatus is a bit more complicated than that employed to measure water-supplying power. Information about the kind of soil and its oxygen content are not primarily needed in this connection. We may employ seed germination to give us some idea of the range of the oxygen requirement for plant roots. The rate of oxygen supply necessary for germination is greater for some kinds of seed than for others and Cannon's excellent work[4] indicates that the requisite rate varies greatly with soil temperature, as would be expected from the nature of respiration. At 22°C. wheat seed failed to germinate well in the Johns Hopkins tests unless the adjacent soil was capable of supplying oxygen at a rate of about 3.0 mg. per hour per square meter of surface. On the other hand, rice seed germinated well in soil that could not supply oxygen at a rate greater than 0.5 mg. per hour per square meter.

We may say that with climatic conditions similar to those of the Baltimore summer, a soil suitable for healthy growth of ordinary upland plants must be capable of supplying water and oxygen at rates not much lower than about 80 g. and 3 mg., respectively, per square meter per hour. This statement emphasizes the importance of both water and oxygen in the soil, for ordinary upland plants, and also the great difference between the dynamic requirements for these two substances. For the climatic conditions of the Baltimore summer the subterranean rate of water supply required for healthy lawn plants is about 27,000 times as great as the rate of subterranean oxygen supply required by wheat seedlings. While a square meter of absorbing root surface appears to need 80 g. of water per hour, the same extent of surface needs only 3 mg. or about 2 ml. of oxygen, or the oxygen content of about 10 ml. of ordinary air.

[1] Hutchins, Lee M., *Plant Physiol.*, **1**, p. 95 (1926).

[2] Livingston, Burton E., and Riichiro Koketsu, *Soil Sci.*, **9**, p. 469 (1920). Mason, T. G., *West Indian Bull.*, **18**, p. 157 (1921). Hardy, F., *Ibid.*, **19**, p. 189 (1922). Livingston, Burton E., and Ichiro Ohga, *Ecology*, **7**, p. 427 (1926). Livingston, Burton E., Takewo Hemmi and J. Dean Wilson, *Plant Physiol.*, **1**, p. 385 (1926).

[3] Hutchins, Lee M., and Burton E. Livingston, *J. Agric. Res.*, **25**, p. 133 (1922). Hutchins, see note 1.

[4] Cannon, William A., *Carnegie Inst. Washington*, Year Book, **20**, p. 48 (1922). *Ibid.*, **22**, p. 56 (1924). *Ibid.*, **24**, p. 289 (1925). *Idem., Science*, **58**, p. 331 (1923). Cannon, William A., and Edward E. Free, *Carnegie Inst. Washington.*, Publ. 368 (1925).

ON THE DISTORTION OF THE CONTINUOUS BACKGROUND BY WIDE ABSORPTION LINES

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In the course of applying photometric methods to spectra in the Harvard collection, data have accumulated on the relative strengths of successive members of the Balmer lines for a number of stars. The present note contains measures for a series of stars representing seven spectral classes ranging from *Od* to *F*0. The loss of light at the center of all available lines was measured for each of the spectra in the usual manner. The measures are internally consistent for each star, but they are not directly comparable from star to star because they were made on plates of different dispersions. To be directly comparable the percentage light losses should be multiplied by an unknown linear factor, which cannot, however, differ greatly from unity. Its precise value does not concern us. The standardization by an arbitrary curve was carried out according to the method described by Hogg,[1] and the consistency of the results for the various members of the Balmer series, when the curve was standardized by the depth of one of them, is a favorable test of the method.

Percentage light losses at the centers of the Balmer lines for eight stars are illustrated in figure 1.

The line depths reach a maximum between $H\delta$ and $H\eta$, and fall off smoothly towards both red and violet. The laboratory intensities of the Balmer lines, as given by Fowler,[2] fall off linearly, $H\beta$ having a value of 9, and $H\zeta$ of 5. These numbers are probably arbitrary, but evidently the early members of the series are the strongest. The fall in the red, which we shall not consider further, has never been generally explained, although Davidovich[3] interpreted certain special stars. Probably incipient emission is the cause of weak $H\beta$ in many spectra,[4] and perhaps the general weakening of lines of longer wave-length[5] is also a contributory factor.

The stars of figure 1 may be divided into two groups according to the rate of fall in the violet of the successive lines. One group contains the supergiants, β Orionis and α Cygni, and the second comprises all the other stars. As suggested to the writer by Miss Williams, there can be no doubt that the apparent rapid falling off of the higher members of the series in the spectra of normal stars is the result of the wings of the lines which are confluent to the violet of $H\zeta$. The lines of the supergiants are winged very slightly, and they, therefore, furnish the best available astrophysical evidence on the relative intensities of the Balmer lines.

The range in ionization temperature represented in figure 1 is from 30,000° or higher for ζ Puppis to 6500° for Canopus, and evidently the change in relative intensity accompanying this five-fold change of temperature is not large. The slopes for β Orionis and α Cygni, stars that differ in temperature by four thousand degrees, are sensibly the same, as may be seen from figure 1. This fact, and the observation that the greater slopes are correlated, not with temperature, but with line width and wingedness, suggests that the true line depths for all stars are in the same ratio as for supergiants, but the wings of the lines of other stars cut down the continuous background so that apparent depths fall off

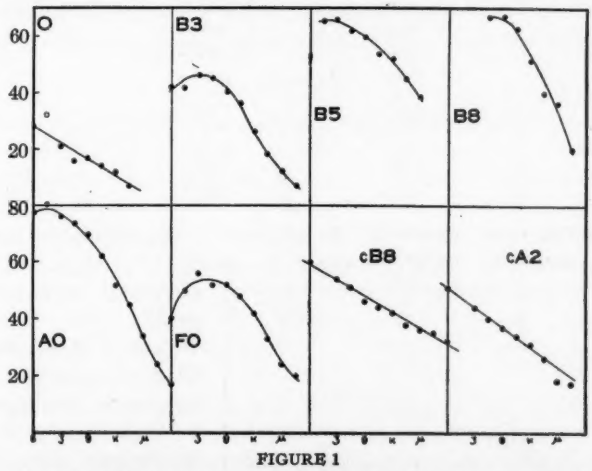

FIGURE 1

Relative intensities of successive Balmer lines (abscissae) expressed in percentage light losses (ordinates) for stars of Class O (ζ Puppis), B3 (α Eridani), B5 (Electra), B8 (Atlas), A0 (Vega), F0 (Canopus), cB8 (Rigel), and cA2 (α Cygni).

more rapidly. The more the lines are crowded toward the limit of the series, the more is the continuous background depressed by the confluence of the wings, until the lines disappear and are replaced by continuous absorption.[6] Some such distortion of the continuous background is evident from the tracing of the spectrum of Electra shown in *Harvard Circular* **303.**

It is of interest to examine the form that the continuous background of a star with heavily winged Balmer lines would take if the relative depths of the lines were the same as those in α Cygni. Material for the study of this question is provided by two plates taken for the purpose of examining the possible variation of the spectrum of α Cygni. The plates were cut from the same piece of glass, exposed intermittently so that they

received equal exposures over the same interval of time, and developed together. Each was standardized by three exposures on Vega, taken with apertures in the ratio 8, 2, 4 (in this order). The reduction curves

TABLE 1

CONTINUOUS BACKGROUND

LINE	α CYGNI	VEGA	DIFF.
γ	58	12	−46
δ	64	18	−46
ε	86	44	−42
ζ	156	115	−41
η	215	174	−41
θ	249	230	−18
ι	274	269	− 5
κ	290	305	+15
λ	306	338	+32
μ	322	368	+46
ν	335	388	+53
ξ	349	405	+54
ο	364	418	+54
π	373	430	+57

were excellent and consistent. In addition to the standards, one plate bore six spectra of Vega, the other six spectra of α Cygni. The sky conditions were unusually good.

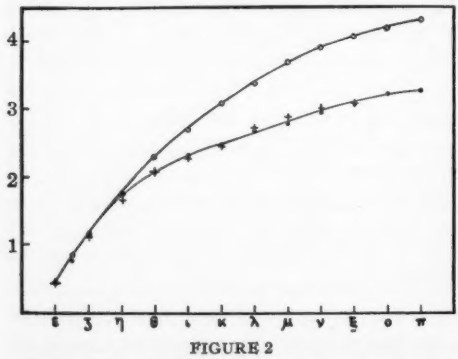

FIGURE 2

Comparison of the continuous backgrounds of α Cygni and Vega in the ultra-violet. Ordinates are magnitudes (numerically larger for smaller light intensities); abscissae are successive Balmer lines. Open circles and dots represent observed backgrounds for Vega and α Cygni; crosses represent the "corrected" background of Vega, taken from the sixth column of table 2.

Table 1 shows the mean relative intensities of the continuous backgrounds for Vega and for α Cygni, the former derived from twelve spectra, the latter from six, expressed in magnitudes. The fourth column gives the difference between columns three and two. This difference is not equal to the difference in photographic magnitude between the two stars because the spectra were photographed with different apertures. It should, however, be constant, as the two stars are at about the same temperature.[7] As may be seen from figure 2, the difference in photographic magnitudes of the backgrounds is not constant after $H\eta$ and it increases to almost a magni-

tude at $H\pi$, the spectrum of Vega being fainter in the violet. The exact point at which the backgrounds begin to differ in energy distribution is difficult to locate because the depression is very small when the wings of the lines are only slightly confluent. It may be placed at about $H\zeta$ from an examination of the tracings, which show the wings of $H\zeta$ and $H\eta$ in contact; probably a plate with greater contrast-sensitivity would show that the point of contact of the wings is even farther to the red, perhaps between $H\epsilon$ and $H\zeta$. If any measures of temperature were made by comparing Vega and α Cygni in the ultra-violet, a higher temperature would be assigned to α Cygni because of the distortion of the background of Vega, which will be discussed later.

Table 2 contains, in successive columns, the line, the depth in the

TABLE 2

LINE	DEPTH IN α CYGNI	MAGNITUDES VEGA	DIFFERENCE	CORRECTED DIFFERENCE	CORRECTED BACKGROUND DIFFERENCE	SUM
K	(102)	(175)	..	..	+ 2	..
$H\zeta$	63	156	93	0	− 7	− 7
$H\eta$	58	146	88	− 4	− 7	−11
$H\theta$	50	130	80	−14	+16	+ 2
$H\iota$	46	105	59	−34	+29	− 5
$H\kappa$	40	80	40	−52	+49	− 3
$H\lambda$	32	65	33	−61	+66	+ 5
$H\mu$	22	46	24	−68	+80	+12
$H\nu$	20	30	10	−82	+87	+ 5
$H\xi$	14	20	6	−86	+88	+ 2
				−86		
				−89		

spectrum of α Cygni and of Vega (expressed in stellar magnitudes), the difference between the two preceding columns, the difference corrected to zero at $H\zeta$, the difference between the continuous backgrounds of the two stars (taken from table 1 and corrected by +0.32), and the sum of the two preceding columns. The correction of +0.32 implies shifting the curves along the axis of ordinates until the best general coincidence is obtained and corrects the background differences so that the mean of the deviations is as small as possible. This shift is legitimate because all the quantities are expressed in stellar magnitudes. The relative line depths and the relative and "corrected" continuous backgrounds are shown in figure 2. The small entries in the last column of the table (mean value, five hundredths of a magnitude) show that if it is assumed that the true relative intensities of the Balmer lines of Vega are the same as for α Cygni, the resulting continuous background for Vega coincides sensibly with that of α Cygni in harmony with their temperatures.

The slight systematic run in the entries of the seventh column is not to be interpreted as a difference of temperature. As higher members of

the series are reached, the relative intensities in α Cygni are also disturbed by the confluence of the wings, and it is not possible to decide at what point we cease to eliminate true distortion and begin to eliminate differential distortion. Furthermore, the effect of continuous absorption sets in well to the red of the series limit, and may be different for the two spectra. The run in the residuals of the last column is most likely, however, to be the result of the systematic difference of altitude.

Brief reference may be made to several aspects of these data. Evi-

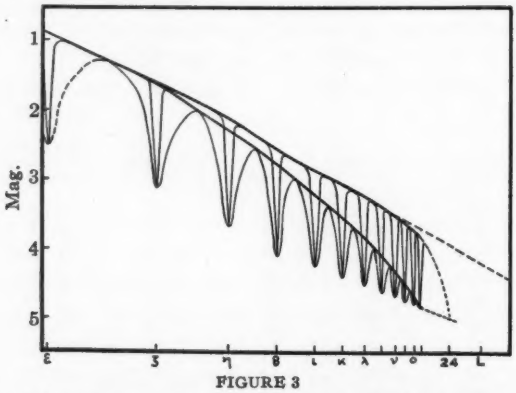

FIGURE 3

Schematic comparison of ultra-violet spectra for stars with narrow and wide lines. The relative depths of the narrow lines are as for α Cygni and the actual depths of the wide lines as for Vega. The observed continuous backgrounds for α Cygni and Vega are represented by the upper and lower heavy lines. The upper broken line shows the possible form of the undistorted continuous background; the curved broken line, the assumed continuous background for the narrow line star; and the lower broken line, the continuous absorption. For the narrow line star, the wings are observed to become confluent between Hμ and Hν.

dently the continuous backgrounds of all stars with strong Balmer lines are distorted in the ultra-violet. Measures of temperature cannot, therefore, be based upon that spectral region. Greaves, Davidson and Martin[7] wisely used no wave-length shorter than 3900 in their spectrophotometric work.

In measuring the color index of a star, the photographic light is integrated. The distortion of the background by heavy absorption must affect systematically the color indices of stars with strong Balmer lines. The effect on color index will be detected in practice not for the normal *A* or *B* star, which always has winged Balmer lines, but for the narrow-lined supergiant. The color indices for hot supergiants should differ

systematically from those of normal stars at the same temperature and should, moreover, more nearly represent that temperature. It should be noted that supergiants tend to have lower temperatures than normal stars *of the same spectral class*, and, therefore, a significant comparison of color indices can be made only for a giant and a supergiant which give the same temperature from spectrophotometric measurements to the red of 3900. No data for making such a comparison are known to the writer. Similarity of spectrum is no guide to the selection of a suitable pair.

The effect of the distortion of background on measurements of color index has a bearing on the investigation of the very luminous apparently faint stars in clusters and Magellanic clouds by means of their color indices. Such stars are likely to be *c*-stars with narrow lines, and their color indices may, therefore, differ systematically from those of nearby stars with spectra assigned to the same class. The *c*-character probably also introduces a systematic difference for the classification of these very distant stars of Class *A*, as pointed out by Shapley, by displacing their apparent spectral class towards *F*. It is, therefore, necessary to evaluate the relative contributions of color index and spectral class; discrepancies between spectral class and color temperature might be expected for these distant stars.

[1] Hogg, *Harv. Obs. Bull.* **856**, 1928.
[2] Fowler, *Report on Series in Line Spectra*, **1922**.
[3] Davidovich, *Harv. Obs. Bull.* **846**, 1927.
[4] Payne and Hogg, *Harv. Obs. Circ.* **303**, 1927.
[5] Payne, *Harv. Obs. Circ.* **307**, 1927.
[6] Wright, *Lick Obs. Bull.* **332**, 1921.
[7] Hertzsprung, *Leiden Ann.*, **14**, 1922 (41); Greaves, Davidson and Martin, *M. N. R. A. S.*, **87**, 1927 (352).

A CASE OF STREAMING IN A VALVE

BY E. BODEWIG

KÖLN, GERMANY

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For the engineer it is a matter of great importance to know the pressure of water against a trap-valve, a problem which seems not yet to have been treated.

We confine ourselves to a special case of a streaming in two dimensions. It is unnecessary to say that every such streaming is represented by a function $f(z)$ of the complex variable $z = x + iy$. Then let

$$f(z) = \varphi(x, y) + i\psi(x, y) \equiv \varphi + i\psi$$
$$w(z) = f'(z) = \varphi_x - i\varphi_y = \psi_y + i\psi_x. \qquad (1)$$

Note that

$$\int w dz = \int (\varphi_x dx + \varphi_y dy) + i \int (-\varphi_y dx + \varphi_x dy) = \int \varphi_s ds + i \int \varphi_n ds = curl\ \varphi + i\ div\ \varphi \qquad (2)$$

all integrals being taken around a closed curve.

Now, let us suppose the following streaming in two dimensions: let a fluid rising from the source of the divergence $2q$ move between an immovable infinite wall and a parallel one, also infinite, being translated perpendicularly to itself with the velocity $c = c(t)$. Suppose further the fixed wall is $y=0$ the movable is $y = h$ and the source is at the origin. Then the conditions on the velocity with the components u and v are

$$\begin{aligned} &v = 0 \quad \text{when } y = 0 \text{ except at the origin} \\ &v = c \quad \text{when } y = h \\ &\int (u dy - v dx) = 2q \end{aligned} \qquad (3)$$

the integral being taken around a curve including the origin.

Let the fundamental equations in hydrodynamics be written:

$$\begin{aligned} \gamma \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) &= - \frac{\partial p}{\partial x}, \\ \gamma \left(\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right) &= - \frac{\partial p}{\partial y}, \end{aligned} \qquad (4)$$

where γ is the density of the fluid and p the pressure.

Then let $\varphi(x, y)$ be an analytic function of x and y. Then the equations above are fulfilled by putting

$$\begin{aligned} u &= \varphi_x,\ v = \varphi_y, \\ p &= -\gamma \left(\varphi_t + \frac{1}{2} (u^2 + v^2) \right). \end{aligned} \qquad (5)$$

Introduce besides φ the stream-function ψ so that

$$w = u - iv,\ f = \varphi + i\psi = \int w dz.$$

With regard to the conditions above, w must be a function regular except at the origin in the whole strip limited by $y = 0$ and $y = h$, and must satisfy the conditions:

$$\left.\begin{aligned} &w \text{ is real for a real variable, except at the origin; } w \text{ is purely imaginary for a purely imaginary variable; } w = u - ic \text{ [where } c \\ &= c(t)\text{]; when } z = x + ih, \int w dz = 2iq. \end{aligned}\right\} \qquad (6)$$

The last equation is stronger than the last one in (3), for it requires further the vanishing circulation. To build this function we make use of the Riemann-Schwarz principle of symmetry. Since, on the straight line

$y = h$, w has a constant imaginary component it can be continued over that line so that at opposite points it has conjugate imaginary values. Then we have a function defined in the strip limited by $y = 0$ and $y = 2h$. It can also be continued over that last line, and so on, so that we get a function with the period $2h$. The fundamental functions of such a kind are $\sin \frac{\pi y}{2h}$ and $\cos \frac{\pi y}{2h}$ or, in our case, $\mathrm{sh} \frac{\pi z}{2h}$ and $\mathrm{ch} \frac{\pi z}{2h}$ where $\mathrm{sh}x$ and $\mathrm{ch}x$ are the hyperbolic functions $-i \sin ix$ and $\cos ix$. Since w is odd and infinite at the origin, it must be a function of $\frac{1}{\mathrm{sh} \frac{\pi z}{2h}}$ or of $\mathrm{cth} \frac{\pi z}{2h}$. As

$$\frac{1}{\mathrm{sh} \frac{\pi z}{2h}} = \frac{2h}{\pi z} - \frac{\pi z}{12h} + \ldots$$

$$\mathrm{cth} \frac{\pi z}{2h} = \frac{2h}{\pi z} + \frac{\pi z}{6h} + \ldots$$

we have now the two functions $\frac{q}{2h} \cdot \frac{1}{\mathrm{sh} \frac{\pi z}{2h}}$ and $\frac{q}{2h} \cdot \mathrm{cth} \frac{\pi z}{2h}$ which satisfy the first, second and last of the conditions of (6). But if we put $z = x + ih$ we see that the latter function has a constant imaginary component, viz., zero, so that by putting

$$w = -\frac{c}{h} z + \frac{q}{2h} \mathrm{cth} \frac{\pi z}{2h}$$

we obtain the desired function.

Streamlines.—Let us consider now the streamlines of motion. Since $w = u - iv$, we have

$$u = -\frac{c}{h} x + \frac{q}{2h} \cdot \frac{\mathrm{sh} \frac{\pi x}{h}}{\mathrm{ch} \frac{\pi x}{h} - \cos \frac{\pi y}{h}} \tag{7}$$

$$v = \frac{c}{h} y + \frac{q}{2h} \cdot \frac{\sin \frac{\pi y}{2h}}{\mathrm{ch} \frac{\pi x}{2h} - \cos \frac{\pi y}{h}}. \tag{8}$$

By integration of w and by a convenient choice of the integration's constant we get

$$f = -\frac{1}{2}\frac{c}{h}z^2 + \frac{q}{\pi}\left[\ln \operatorname{sh}\frac{\pi z}{2h} - \frac{i\pi}{2}\right] \tag{9}$$

$$\psi = -\frac{c}{h}xy - \frac{q}{\pi}\operatorname{arc\,ctg}\left(\operatorname{cth}\frac{\pi x}{2h}\cdot\operatorname{tg}\frac{\pi y}{2h}\right). \tag{10}$$

Here, arc ctg has the same sign as x and varies between $-\frac{\pi}{2}$ and $+\frac{\pi}{2}$. The straight line $x = 0$ is the streamline $\psi = 0$. In this manner no streamline $\psi \neq 0$ can meet the straight line $x = 0$ otherly than at the origin. That is, an infinite number of streamlines comes from the source $z = 0$. Since in its neighborhood, $\operatorname{cth}\frac{\pi x}{2h}\cdot\operatorname{tg}\frac{\pi y}{2h} = \frac{y}{x}$, ψ has, on these streamlines, the value $q\frac{\alpha}{\pi}$ where α is the positively taken angle of the streaming direction and $x = 0$. For these streamlines, therefore, is $|\psi| < \frac{q}{2}$ and ψ has the contrary sign as x.

In the following we consider only positive values of α, the streaming being symmetrical to $x = 0$.

From the equations (7), (8), (10) we draw the conclusions

$$\left.\begin{aligned} u &= -\frac{c}{h}x + \frac{q}{2h}\cdot\operatorname{cth}\frac{\pi x}{2h} \\ v &= 0 \end{aligned}\right\} \text{when } y = 0 \tag{11.1}$$

$$\left.\begin{aligned} u &= -\frac{c}{h}x + \frac{q}{2h}\cdot\operatorname{th}\frac{\pi x}{2h} \\ v &= c \end{aligned}\right\} \text{when } y = c. \tag{11.2}$$

$$\psi = -cx \quad \text{when } y = h \tag{11.3}$$

$$\left.\begin{aligned} u &= 0 \\ v &= \frac{c}{h}y + \frac{q}{2h}\cdot\operatorname{ctg}\frac{\pi y}{2h} \end{aligned}\right\} \text{when } x = 0. \tag{11.4}$$

Hence, we have the following results:

The x-axis is a streamline. (12.1)

At the valve the vertical velocity is constantly c. (12.2)

All streamlines coming from the source either meet or do not meet the valve according as $c>0$ or $c<0$, since near the source always $\psi<0$. (12.3)

The y-axis is a streamline. (12.4)

These results are valid for *every* streaming. But for a closer inquiry two cases are to be distinguished: $c<0$, $c>0$.

I. $c<0$. *Case of Shutting Valve.*—In this case we have:

$$\psi = -cx, \text{ when } y = h. \tag{13.1}$$

Vanishing of u and v is only possible if $x = 0$. Then y is determined by

$$2cy + q.\text{ctg}\frac{\pi y}{2h} = 0 \text{ (cf. 11.1 and 11.4).} \tag{13.2}$$

$$u = \frac{|c|}{h}x + \frac{q}{2h} \text{ when } x \text{ is very great.} \tag{13.3}$$

$$v = -\frac{|c|}{h}y \text{ when } x \text{ is very great.} \tag{13.4}$$

Should ψ be a constant k it results from (11) that

$$y = h.\frac{2k+q}{2|c|x}, \text{ when } x \text{ is very great.} \tag{13.5}$$

From this we draw the conclusions:

Not one streamline coming from the source meets the trap-valve. (14.1)

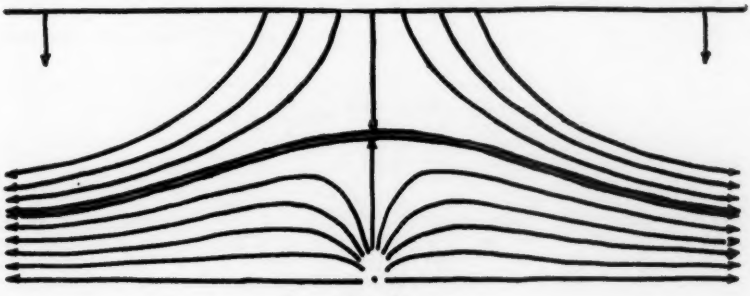

FIGURE 1

There is, on the y-axis, a singular point at which the velocity is zero. At this point water coming from valve meets water rising from the source. (14.2)

The fluid runs always to the right and the more rapidly the greater is the distance from the source. (14.3)

For sufficiently great values of x fluid is streaming towards the fixed wall. (14.4)

All streamlines approach asymptotically the x-axis as does a hyperbola, especially the second streamline $\psi = 0$ which crosses rectangularly the y-axis at the singular point of (14.2). This streamline separates the water of the source from that of the trap-valve. (14.5)

So we have figure 1.

II. $c>0$. *Case of Opening Valve.*

$$v>0 \text{ (cf. 8)} \tag{15.1}$$

$$u = -\frac{c}{h}x + \frac{q}{2h} \text{ when } x \text{ is very great.} \tag{15.2}$$

$$v = \frac{c}{h}y \text{ when } x \text{ is very great.}$$

Should $u = 0$ then must $y = 0$ and $x = \frac{q}{2c} \cdot \operatorname{cth} \frac{\pi x}{2h}$. (15.3)

or

$$y = h \text{ and } x = \frac{q}{2c} \cdot \operatorname{th} \frac{x\pi}{2h}.$$

Generally, $u = 0$ for points satisfying the equation

$$\cos \frac{\pi y}{h} = \operatorname{ch} \frac{\pi x}{h} - \frac{q}{2cx} \cdot \operatorname{sh} \frac{\pi x}{h}. \tag{15.4}$$

Let

$$u = -\frac{c}{h}x + \frac{q}{2h} \cdot \frac{\operatorname{sh} \frac{x\pi}{h}}{\operatorname{ch} \frac{\pi x}{h} + s} \tag{15.5}$$

then

$$\frac{du}{ds} = -\frac{q}{2h} \cdot \frac{\operatorname{sh} \frac{\pi x}{h}}{\left(\operatorname{ch} \frac{\pi x}{h} + s\right)^2} < 0.$$

That is to say:

All streamlines rising from the source meet the trap-valve. (16.1)

For sufficiently great values of x water comes running out of the infinite with a velocity growing proportionally to x. (16.2)

On the x-axis, there is always a singular point of vanishing velocity. (16.3)

The two walls are perpendicularly met by the curve

$$y = \frac{h}{\pi} \cdot \operatorname{arc} \cos\left(\operatorname{ch} \frac{\pi x}{h} - \frac{q}{2cx} \cdot \operatorname{sh} \frac{\pi x}{h}\right)$$

for there $y' = \infty$. At each of their points, the curve is crossed vertically by the streamlines. (16.4)

x being constant and y growing the velocity u decreases! That is, the

curve mentioned goes from above to the left downwards to the right. In the part enclosed by the fixed wall and the curve water goes away from the

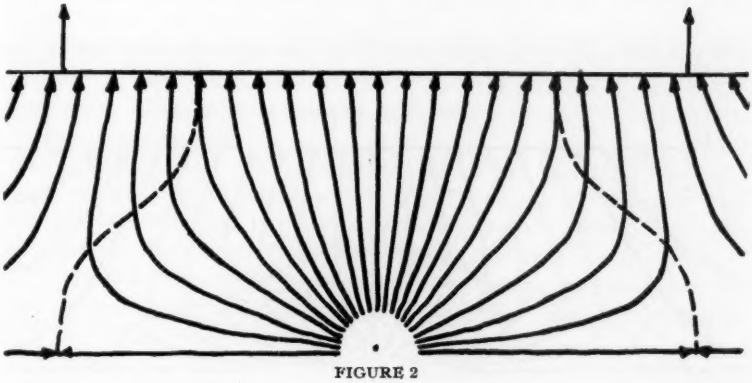

FIGURE 2

middle, in the part enclosed by the movable wall and the curve it runs towards the middle. (16.5)

The second equation of (15.3)

$$x = \frac{q}{2c} \cdot \text{th} \frac{\pi x}{2h}$$

has a solution only if $\frac{\pi q}{4hc} > 1$. For the curve $\xi = \frac{q}{2c} \cdot \text{th} \frac{\pi x}{2h}$ has the gradient $\frac{q\pi}{4hc} \cdot \frac{1}{\text{ch}^2 \frac{\pi x}{2h}} > 0$, that is, at the origin $\frac{\pi q}{4hc}$.

So *two cases* are again to be distinguished

$$(a)\ \frac{\pi q}{4hc} > 1.$$

If $y = h$, u and $\frac{du}{dx}$ are at first positive, later negative (Fig. 2).

$$(b)\ \frac{\pi q}{4hc} < 1.$$

At the trap-valve $y = h$ is always $u < 0$ and $\frac{du}{dx} < 0$.

The curve (Fig. 3) above crosses the y-axis at the point determined by

$$y = \frac{h}{\pi} \cdot \text{arc cos} \left(1 - \frac{\pi q}{2ch}\right).$$

There is still a difficulty in the preceding: One must consider that all the

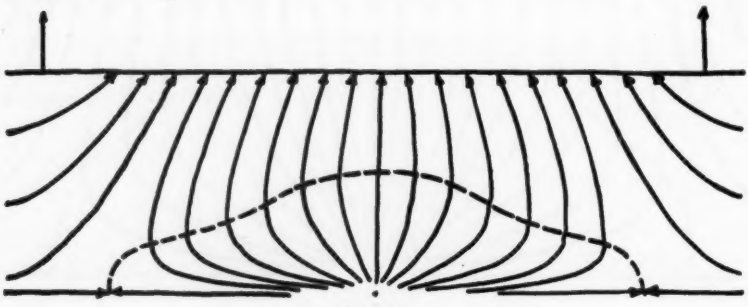

FIGURE 3

streamlines always spoken of are not real; that is, they are not constant, but, the trap-valve moving, they *change* every moment since c and h are functions of t. These real streamlines shall, perhaps, be discussed in a later article.

STUDIES ON BIOCHEMICAL DIFFERENCES BETWEEN SEXES IN MUCORS

5. Quantitative Determinations of Sugars in (+) and (−) Races[1]

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The presence in fungi of some soluble carbohydrates, such as trehalose and glycogen, and of the carbohydrate alcohol mannit, which are seldom found in other plants, and the absence of cane sugar and starch is characteristic of this group of plants. Bourquelot,[2] in a series of experiments, has shown a close relation between trehalose and mannit in various higher fungi. This disaccharide is converted into mannit extremely rapidly during desiccation of the fungus. A number of analyses have also shown that the amount of trehalose is greater at the beginning of fructification and that it decreases or disappears entirely when the fungi have become mature.[3] The reverse was found to be true of the mannit. Most of these tests were made with higher fungi and our present knowledge of the

carbohydrates in Mucors is slight. Little is reported in the literature concerning the interrelationship between various carbohydrates in the Mucors or concerning the amount of sugars in this group. The investigation which is here reported was undertaken in a study of the biochemical differences between sexes, but it offers, as well, data upon the presence of sugars in various species of Mucors. The occurrence of various carbohydrases in different species in this group of fungi has been discussed in a previous publication.[4]

In a series of tests with various species, as well as with a relatively large number of races belonging to a single species, the amount of total soluble, of reducing, and of non-reducing sugars was determined in cultures at a certain stage of development. The species and races investigated were selected from those previously tested by the reduction reaction with tellurium salts and were chosen so that there were representatives of both strong and weak reducers among those tested.

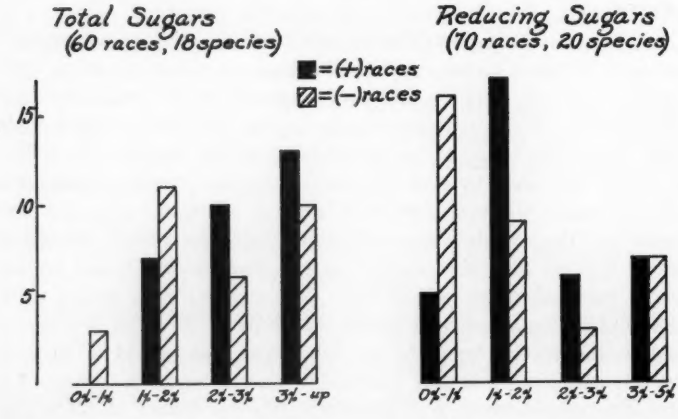
It seemed possible from these experiments to obtain information in regard to: (1) the relative amounts of sugars characteristic of the different species; (2) the relative amounts of sugars in (+) and (−) races; (3) the relation of the reducing sugars to the greater average reducing capacity previously found to be characteristic of the (+) sex.[5,6,7]

Great care was taken to have the material as far as possible comparable. Paired (+) and (−) races were cultivated at the same time and under the same conditions, each in several Erlenmeyer flasks, and all the manipulations of a given pair were carried on simultaneously. Equal amounts of spores were taken for inoculation. The cultures were grown on our No. 230 nutrient medium and incubated at 26°C. for 6 to 8 days, according to the species tested.[8] At the end of this period of time, the fungus felt was harvested and thoroughly washed under a stream of tap water. The excess water was absorbed between sheets of filter paper before the mycelia were weighed. The weight varied from 10 to 20 grams. To avoid possible action of enzymes upon the carbohydrates during drying, the sugars were extracted from fresh mycelia, but dry weights were determined from aliquot samples. For the method used in preparing the extracts, we are indebted to Dr. Hasselbring of the U. S. Bureau of Plant Industry.

The fresh mycelium, to which a small amount of powdered $CaCO_3$ was added, was extracted in a water bath with boiling 70% alcohol for 10 minutes. This was repeated 3 to 4 times with fresh alcohol. The mycelium was then carefully washed on the filter with hot alcohol. The extracts of both tested races were brought to the same volume and transferred to 2 similar standardized beakers and evaporated to about 20 cc. over a steam bath. These concentrated extracts were transferred to flasks to which were added the measured amounts of hot water used in

rinsing the beakers in which evaporation had taken place. These mixtures were clarified with a saturated solution of neutral lead acetate and filtered through a small amount of animal charcoal according to the method mentioned by Spoehr.[9] Without the charcoal, filtration took place with great difficulty because of the clogging of the filter paper. To remove the excess of lead in the filtrate, dry sodium oxalate was added. After several filterings, clear and colorless sugar solutions were obtained. The two filtrates were brought to the same volume and each was divided into two portions. One was used for the determination of the reducing sugars. From the other, the total soluble and non-reducing sugars were determined after hydrolysis by enzymes prepared by Harang's method.[10] The

Fig. 1



difference in the amounts of reducing sugars before and after hydrolysis showed the amount of non-reducing sugars. The determinations were made by the volumetric method of MacLean[11] which permits a determination of very small amounts of sugar with considerable accuracy. Since each determination required only about 1 cc. of the extract, it was possible to repeat the tests. Such repetitions were usually made and showed close agreement. Standardizations were made by means of Kahlbaum's pure dextrose and by sucrose supplied by the U. S. Bureau of Standards.

The amount of reducing sugars was determined in 70 (+) and (−) races included in 20 species and 11 genera and that of the total and of the non-reducing sugars in 60 (+) and (−) races included in 18 species and 10 genera.

The results which are expressed in terms of glucose and which are based

TABLE 1

PER CENT CONTENT OF WATER IN FRESH MYCELIUM AND OF SUGARS AND FAT CALCULATED ON DRY WEIGHT IN PAIRED RACES OF DIFFERENT SPECIES

SPECIES	SEX	TOTAL SUGARS	% EXCESS	REDUC. SUGARS	% EXCESS	NON-REDUC. SUGARS	% EXCESS	FAT	% OF WATER
Mucor mucedo	(+)	8.10	8.1	4.05	30.7	4.05		2.9	89.8
	(−)	7.45		3.10		4.35	**7.4**	2.0	90.5
Mucor dispersus	(+)	2.40		1.80		0.60		10.6	83.7
	(−)	3.54	**47.5**	2.27	**26.1**	1.27	**111.7**	8.1	88.0
Mucor gris.-cy.*	(+)	3.89	88.8	2.22	115.5	1.67	62.1	6.5	92.0
	(−)	2.06		1.03		1.03		6.0	93.5
Mucor N	(+)	4.77		4.77		0		2.1	84.6
	(−)	5.43	**13.8**	5.43	**13.8**	0		2.9	85.3
Mucor 4	(+)	3.44	67.0	1.93	244.6	1.51	0.7	3.6	88.8
	(−)	2.06		0.56		1.50		5.6	91.5
Mucor 5	(+)	3.07	46.2	0.97	102.1	2.10	29.6	22.2	87.5
	(−)	2.10		0.48		1.62		19.4	87.3
Mucor 7	(+)	1.91	12.3	0.63		1.28	54.2	3.5	92.6
	(−)	1.71		0.88	**39.7**	0.83		8.5	90.7
Rhizopus nigri.*	(+)	2.63		1.82		0.81		5.3	77.6
	(−)	3.59	**36.5**	2.28	**25.3**	1.31	**61.7**	7.2	85.6
Absidia glauca	(+)	1.69		1.18	306.9	0.51		18.2	81.4
	(−)	...		0.29		..		19.5	78.9
Absidia "whorled"	(+)	1.49	181.1	1.49	186.5	0		17.3	84.5
	(−)	0.53		0.52		0		21.8	80.7
Phyco. blakes.*	(+)	4.42	11.6	1.99	36.3	2.43		15.7	85.6
	(−)	3.96		1.46		2.50	**2.9**	22.1	84.7
Circin. umbell.*	(+)	6.48	49.7	5.60	29.6	0.88	∽	6.7	84.0
	(−)	4.33		4.32		0		7.4	79.6
Circin. spinosa*	(+)	3.73	248.6	1.86	588.9	1.87	134.0	12.8	79.9
	(−)	1.07		0.27		0.80		21.9	74.5
Helicos. pirifor.*	(+)	4.80		3.90	25.8	0.90		7.0	83.7
	(−)	5.07	**5.6**	3.10		1.97	**118.9**	9.1	82.7
Blakes. trisp.*	(+)	2.28	55.1	0.98	34.3	1.30	75.7	22.1	81.1
	(−)	1.47		0.73		0.74		15.1	79.8
Choan. cucurbit.*	(+)	2.55	44.1	1.09		1.46	∽	16.9	90.9
	(−)	1.77		1.77	**62.4**	0		6.2	90.6
Syncephalastrum	(+)	...		4.69	18.1	..		12.9	85.3
	(−)	...		3.97		..		12.1	83.4
Parasit. simplex*	(+)	12.68	12.9	3.96	0.8	8.72	**19.5**	6.1	86.2
	(−)	11.23		3.93		7.30		7.2	86.9

* The unabbreviated names of species are: Mucor griseo-cyanus, Rhizopus nigricans, Phycomyces blakesleeanus, Circinella umbellata, Circinella spinosa, Helicostylum piriforme, Blakeslea trispora, Choanephora cucurbitarum, Parasitella simplex.

on calculations of the weight of dry mycelia are shown in tables 1 and 2. The amount of reducing sugars is not high. It is only in 14 races (7 (+) and 7 (−) races) that it exceeds 3 per cent, the highest percentage being a little over 5 per cent (Circinella umbellata (+) and Mucor N (−)). In several races the amount of reducing sugars was less than 1 per cent (5 (+) and 16 (−) races). These relations are shown graphically

TABLE 2

PER CENT CONTENT OF WATER IN FRESH MYCELIUM AND OF SUGARS AND FAT CALCULATED ON DRY WEIGHT IN PAIRED RACES OF CUNNINGHAMELLA BERTHOLLETIAE AND ABSIDIA BLAKESLEEANA

RACES	SEX	TOTAL SUGARS	% EXCESS	REDUC. SUGARS	% EXCESS	NON-REDUC. SUGARS	% EXCESS	FAT	% OF WATER
				Cunninghamella bertholletiae					
217	(+)	7.09	61.5	3.55	126.1	3.54	25.5	22.0	77.1
266	(−)	4.39		1.57		2.82		20.6	77.8
268	(+)	1.22		0.85		0.37	236.4	12.7	78.8
721	(−)	1.63	**33.6**	1.52	**78.8**	0.11		15.7	81.6
465	(+)	1.32		0.77		0.55	129.2	14.0	81.8
240	(−)	1.67	**26.5**	1.43	**85.7**	0.24		14.5	83.3
218	(+)	3.00	31.0	2.45	42.4	0.55	3.5	13.5	85.3
216	(−)	2.29		1.72		0.57		12.8	82.6
779	(+)	2.33	92.6	1.59	189.1	0.74	12.1	19.5	80.5
180	(−)	1.21		0.55		0.66		16.4	78.3
				Absidia blakesleeana					
364	(+)	3.75		2.41		1.34	22.9	21.2	80.2
371	(−)	4.21	**12.3**	3.12	**29.5**	1.09		16.5	82.9
345	(+)	2.75	88.4	2.75	212.5	0		7.2	77.4
715	(−)	1.46		0.88		0.58		21.7	80.7
366	(+)	2.65	56.8	1.89	182.1	0.76		11.4	82.4
363	(−)	1.69		0.67		1.02	**34.2**	19.2	71.8
359	(+)	2.74	5.0	2.49	30.4	0.25		18.5	80.5
811	(−)	2.61		1.91		0.70	**220.0**	20.3	74.8
716	(+)	1.52	67.0	1.25	145.1	0.27		9.5	85.0
365	(−)	0.91		0.51		0.40	**48.2**	9.9	81.7
203	(+)	..		2.25	64.2	..		8.1	79.6
572	(−)	..		1.37		..		13.8	76.6
369	(+)	1.42	79.8	1.22	84.9	0.20	53.9	14.1	75.6
571	(−)	0.79		0.66		0.13		19.7	81.1
355	(+)	2.32		1.01	53.0	1.31		15.3	81.9
717	(−)	..		0.66		..		17.7	80.5
714	(+)	1.76	12.1	1.15	94.9	0.61		13.2	82.9
711	(−)	1.57		0.59		0.98	**60.7**	13.1	80.5
351	(+)	2.64		1.22		1.42	149.1	21.4	77.2
713	(−)	2.88	**9.1**	2.31	**89.3**	0.57		9.1	84.9
370	(+)	2.77	125.2	1.76	81.4	1.01	288.5	..	82.3
367	(−)	1.23		0.97		0.26		..	80.7
201	(+)	..		1.62	165.6	..		..	81.1
349	(−)	..		0.61		..		..	78.7

in figure 1 where the races are arranged in groups according to the amount of sugar present. The average amount of reducing sugar in the 35 (−) races is 1.60 per cent, while that in the 35 (+) races is 2.18. The (+) shows an average excess of 36.25 per cent over the (−) sex.

A comparison of the data from the paired (+) and (−) races shows that, in the majority of the species tested, the (+) races contain a greater quantity of sugars than the (−) races. Tests with a rather large number

TABLE 3

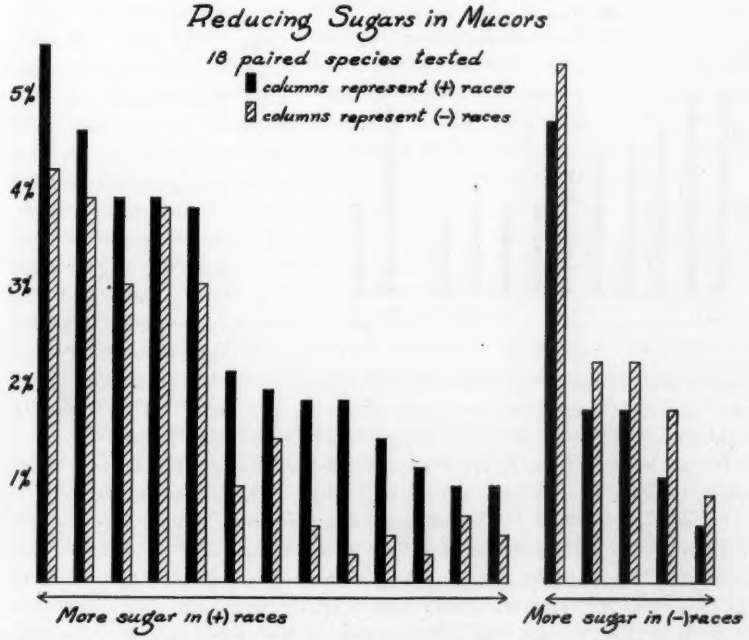
ABSIDIA BLAKESLEEANA

Effect of cultural conditions on fat content

		WELL-DEVELOPED SKIN			WELL-DEVELOPED AERIAL HYPHAE AND SPORANGIA		
RACES	SEX	HEIGHT IN CM.	% OF WATER	% OF FAT	% OF FAT	% OF WATER	HEIGHT IN CM.
355	(+)	0.2	77.1	27.4	15.3	81.9	1.2
717	(−)	0.2	72.5	30.4	17.7	80.5	1.2
714	(+)	0.4	75.6	23.4	13.2	82.9	0.8
711	(−)	0.2	71.1	32.0	13.1	80.5	0.6
370	(+)	0.6	83.3	15.8	13.0	82.3	0.8
367	(−)	0.3	76.1	30.4	21.0	80.7	0.4
201	(+)	0.2	76.5	21.2	12.5	81.1	0.8
349	(−)	0.2	70.9	29.3	22.6	78.7	0.7

of races belonging to a single species (24 (+) and (−) races of Absidia blakesleeana) lead to the same conclusion. This difference is shown in

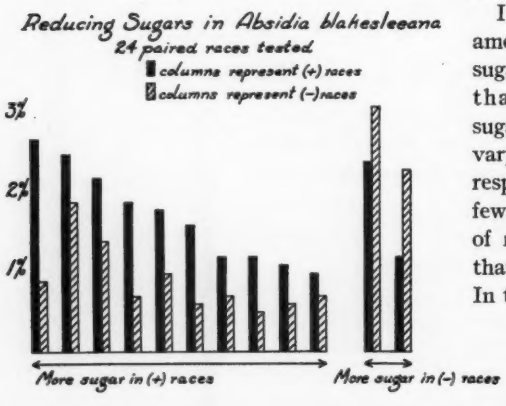
Fig. 2



figures 2 and 3 in which the tested pairs are arranged in two unequal groups according to whether the quantity of reducing sugar is greater in the (+) or in the (−) sex. It has been found that in 74.3 per cent of the cases a greater amount of reducing sugars was present in the (+) race.

The differences found in the amounts of reducing sugars between the (+) and (−) races cannot be held primarily responsible for the differences previously demonstrated in the capacity of the alcoholic extracts of the two sexes to reduce $KMnO_4$. Such low concentrations of sugar as were found would act but slowly on the $KMnO_4$. It should be remembered that our figures here are based on dry weights but that the extracts used in the $KMnO_4$ reaction were obtained from fresh mycelia. The small amount of reducing sugars in these extracts, therefore, would not have given the strong reduction reactions which took place in our previous tests. It may be possible in a later paper to present evidence that the reduction of $KMnO_4$ is chiefly brought about by the presence in Mucors of some substances which may be related to the group of tannins.

Fig 3



In certain cases the amount of total soluble sugars was much higher than that of reducing sugars. Different species vary considerably in this respect. It was only in a few cases that the amount of reducing sugars equalled that of the total sugars. In these cases all the non-reducing sugars may have been already hydrolyzed. A rather high amount of total sugars was found in the races of the parasitic form Parasitella[12] ((+) race about 12 per cent, (−) race about 11 per cent). This excess in total sugars is due to the large amounts of non-reducing sugars.

It can be seen from figure 1 that there are more (+) than (−) races which contain over 2 per cent of total sugar, (23 (+) races against 16 (−) races), while the (−) races are more numerous among those which contain less than 2 per cent (14 (−) races against 7 (+) races). The amount of total sugars in the (+) races averages 3.40 per cent, while in the (−) races it averages 2.60 per cent. This is an excess of 30.77 per cent in favor of the (+) sex. In 73.4 per cent of the cases, the (+) race contains more total sugars than the (−).

The average amount of non-reducing sugars is 1.21 per cent in the (+) races and 0.97 per cent in the (−) races. This shows 24.75 per cent excess of the (+) over the (−) sex. The amount of these sugars varies

very much in different species and in some of them non-reducing sugars are entirely absent. It is in 66.7 per cent of the cases that the amount of non-reducing sugars was higher in the (+) than in the (−) races.

The data obtained from these quantitative sugar analyses have shown that in the majority of the tested pairs larger amounts of total soluble, of reducing and of non-reducing sugars were present in the (+) races. The calculated per cent excess is given in tables 1 and 2. In plants, sugars are of fundamental importance as structural elements and in relation to physiological processes. Too little is known regarding the intra- and interrelationships of carbohydrates, fats and other substances in Mucors to warrant as yet an interpretation of the evident differences which have been discovered. At present, therefore, it seems unwise to stress unduly the apparent connection between these rather unstable substances and sex. The data presented, however, do form a contribution, we believe, towards the solution of the fundamental problem of the biochemical differences between sexes.

Summary.—1. The amounts of total soluble, of reducing and of non-reducing sugars were determined for various Mucors species.

2. Determinations were made in pairs, each pair containing a (+) and a (−) race of a given species in order to compare the amounts of sugar present in the two sexes. The reducing sugars were determined in 70 (+) and (−) races included in 20 species and 11 genera and the total and the non-reducing sugars, in 60 (+) and (−) races included in 18 species and 10 genera.

3. In the majority of the pairs tested, more sugar was found in the (+) than in the (−) races. Thus, the reducing and the total sugars were greater in the (+) races in about 74 per cent of the cases and the non-reducing sugars in about 66 per cent of the races. The average for (+) races was also higher for all kinds of sugars.

4. The amount of reducing sugars present, however, is not sufficient to be chiefly responsible for the reduction reaction previously demonstrated with $KMnO_4$.

5. Other substances, possibly related to the tannins, may be the main cause of the evident differences in reduction capacity of (+) and (−) races.

Addenda.—In connection with estimation of sugars, gravimetric tests were also made for fat content in the same mycelia, using the portion of mycelium set aside for the determination of water content. The results have been computed in percentages of dry weight and are shown in tables 1 and 2. The amount of fat present is relatively large but it is obvious from the figures given that no close connection can be drawn between the sex of the paired races and their fat content. Kordes[13] compared the microscopic appearance in respect to fat content in single pairs of races from 5 species of Mucors and also failed to find differences connected with sex.

There are a number of reasons which render the determination of fat in Mucors unsatisfactory. The method of extraction with petrol ether employed is probably less accurate than the saponification method.[14] A more serious difficulty encountered, however, is the extreme variability of the fungus in respect to fat content under different environmental conditions. Thus a thick sowing of spores leads to the production of a thick mycelial skin and a suppression of aerial hyphæ.

As shown in the adjoining table 3, an increased fat content is associated with a thick skin and a low aerial growth. By changing the conditions of growth of the same race, the amount of fat may be more than doubled. It has been found, moreover, that races, even of the same sex, differ in respect to their tendency to form a skin or aerial hyphæ under similar conditions of growth. Although the conditions of growth have some influence on sugar content, this effect appears to be less marked. Increase of mycelial skin tends also to increase sugar content but in cases tested (5 pairs) the superiority of one sexual race over its paired mate was not materially altered. In view of the care taken to have the paired races as far as possible comparable, we believe that the differences found in relative amounts of sugars in (+) and (−) races are significant.

[1] This investigation was carried on under joint support of the Carnegie Institution of Washington and the Committee of the National Research Council for Research on Sex Problems, to whom the authors gratefully acknowledge their indebtedness.

[2] Bourquelot, B., *Bull. Soc. Myc. France*, **7**, 5 (1891).

[3] Czapec, F., *Biochem. d. Pflanzen.*, G. Fisher, 3 Aufl., **1**, 299 (1922).

[4] Satina S., and Blakeslee, A. F., these PROCEEDINGS, **14**, 229 (1928).

[5] Satina, S., and Blakeslee, A. F., *Ibid.*, **11**, 528–534 (1925).

[6] Satina, S., and Blakeslee, A. F., *Ibid.*, **12**, 191–202 (1926).

[7] Satina, S., and Blakeslee, A. F., *Ibid.*, **13**, 115–122 (1927).

[8] The age of the mycelium has an influence on the amount of sugars which it contains. Thus, in certain species young mycelia showed a relatively small amount especially of reducing sugars at 5 days of growth with no significant differences between the paired races, whereas after 8 days growth the sugar content was materially increased and a distinct difference was found between the races in sugar content.

[9] Spoehr, H., "The Carbohydrate Economy of Cacti," *Carnegie Inst. Washington. Pub.* No. **287**, p. 28 (1919).

[10] These enzymes were obtained from cultures of Aspergillus niger, kindly supplied by Dr. Thom of the U. S. Bureau of Chemistry. For details of the method, see Abderhalden, *Handbuch der biol. Arbeitsmeth.*, Abt. 1, T. 5, Heft 1, p. 93.

[11] MacLean, *Bioch. J.*, **13**, 135 (1919).

[12] The reasons for the provisional assignment of the terms (+) and (−) to the sexual races of Parasitella, despite the apparent impossibility of obtaining a direct sexual reaction with (+) and (−) races of other species, are given in an earlier publication, Satina, S., and Blakeslee, A. F., these PROCEEDINGS, **12**, 202–207 (1926).

[13] Kordes, H., *Bot. Archiv.*, **3**, 282–311 (1923).

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REFLECTION OF ELECTRONS BY A CRYSTAL OF NICKEL

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Continuing our investigation of the interaction between a beam of electrons and a crystal of nickel (*Phys. Rev.*, **30**, 705 (1927)) we are now directing the electron beam against a {111}-face of the crystal at various angles of incidence, and are measuring the intensity of scattering in the incidence plane as a function of bombarding potential and direction.

We find that under certain conditions a sharply defined beam of scattered electrons issues from the crystal in the direction of regular reflection. This occurs whenever the speed of the incident electrons is comprised within any of certain ranges which change in location as the angle of incidence is varied. Within each of these ranges there is an optimum speed at which the intensity of the reflected beam attains a maximum.

That regular selective reflection of electrons from a crystal face would be observed under appropriate conditions was anticipated from our earlier observations on electron diffraction. The phenomenon is clearly the analogue of the regular selective reflection of x-rays on which the Bragg method of x-ray spectroscopy is based, and is, of course, to be interpreted in terms of the undulatory theory of mechanics. The incident beam of electrons of speed v is equivalent to a beam of waves of wave-length h/mv; a portion of the incident beam is regularly reflected, through the process of coherent scattering, from each of the layers of atoms lying parallel to the crystal face, and the intensity of the resultant beam is a maximum when the elementary beams proceeding from the individual layers emerge from the crystal in phase. The condition for such a maximum in the case of x-ray reflection is that the wave-length and angle of the incident beam be related to the separation between successive atom layers of the crystal through the Bragg formula $n\lambda = 2d \cos \Theta$. The condition in the case of electron reflection is somewhat different. The wave-length $\lambda(=h/mv)$ of the reflected beam at maximum intensity is not given by the Bragg formula.

These results, including the failure of the data to satisfy the Bragg formula, are in accord with those previously obtained in our experiments on electron diffraction. The reflection data fail to satisfy the Bragg relation for the same reason that the electron diffraction beams fail to coincide with their Laue beam analogues. These differences between the electron and x-ray phenomena can perhaps be accounted for by assuming, as first suggested by Eckart,[1] that the crystal is characterized by an index of refraction for electrons as it is for x-rays, and that for elec-

trons of the speeds used in our experiments the index has values which are quite different from unity.

The present experimental arrangement is indicated in the schematic diagrams of figure 1. The face-centered cubic array of atoms in the nickel crystal (1-*a*) has been cut through at right angles to one of the cube diagonals to expose a triangular {111}-face (1-*b*). The incident beam of electrons is directed against this face and lies in the quadrant bounded

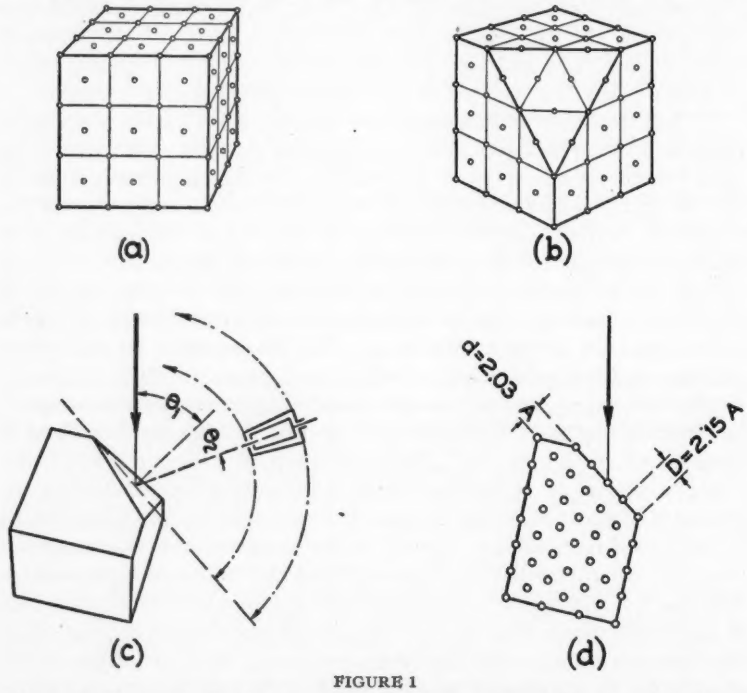

FIGURE 1

Schematic diagrams indicating the experimental arrangement for measuring the reflection of electrons.

by the normal to the crystal face and a line from the center of the triangle through one of the apexes (1-*c*). (In our previous notation the incident beam lies in one of the {111}-azimuths of the crystal.) The angle θ_1 between the incident beam and the normal to the crystal face is adjustable, and the collector can be moved about in the plane of incidence. Unfortunately, the insulation between the parts of the collector is not so high as it should be, and we are unable for this reason to use a retarding potential to stop off the low-speed secondary electrons. We are obliged, for the present, to accept into the collector electrons of all speeds.

The atoms in the crystal lie in lines which cut the plane of incidence as indicated in (1-*d*). The crystal may be regarded as made up of plane gratings lying parallel to the crystal face. The constant of these gratings is 2.15 Å and the separation between adjacent gratings is 2.03 Å.

The location of the incident beam in one of the principal azimuths of the crystal is of no importance, of course, so far as observations on the

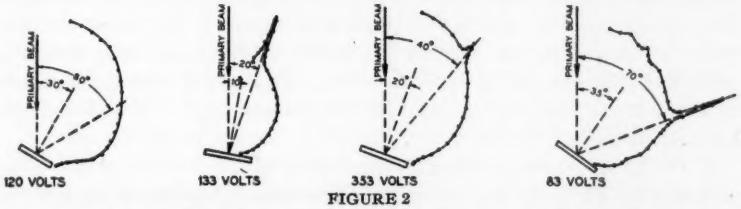

FIGURE 2

Distribution-in-angle of electrons of all speeds issuing from a [111] face of a nickel crystal for various angles of incidence and speeds of bombardment.

regularly reflected beam are concerned. This adjustment was made for the purpose of bringing some of the strong diffraction beams into the plane of incidence, and, therefore, into the range of observations. Such beams are found and have been used to calculate electron wave-lengths. The reflection beams cannot be used for this purpose.

In figure 2 we show distribution-in-angle curves for electrons of all speeds for various combinations of angle of incidence and bombarding

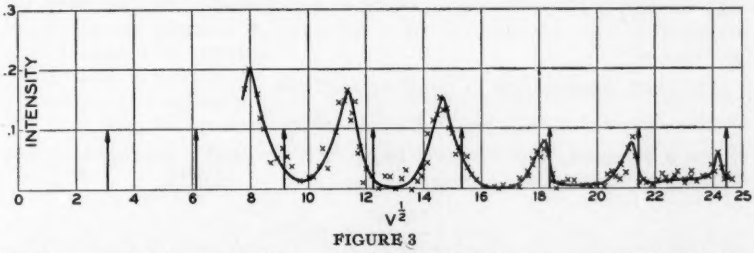

FIGURE 3

Variation of the intensity of the regularly reflected electron beam with bombarding potential, for 10° incidence—Intensity vs. $V^{1/2}$.

potential. The first curve is included to show that under certain conditions the intensity of the regularly reflected beam is immeasurably low. The sharp spurs which characterize the other curves reveal the reflected beam at one or another of its intensity maxima. The axes of these spurs appear to lie accurately in the direction of regular reflection. The angles of incidence and reflection are in all cases the same to within half a degree by our scale readings, and this is within the limit of uncertainty of the measurements.

In figure 3 we have plotted the intensity of the reflected beam for angle of incidence 10 degrees—or rather, a certain function of this intensity—against the square root of the bombarding potential. What is plotted as ordinate is one less than the ratio of the current received by the collector standing in the direction of regular reflection to the mean of the currents received in two adjacent directions, one on each side of the beam. The curve cannot be extended much below $V^{1/2} = 8$ because of limitations of the apparatus; the current of the incident beam is too small to work with for bombarding potentials much below 65 volts. By measurements made in a different way we have, however, an indication that the regularly reflected beam has another intensity maximum near $V^{1/2} = 5.3$ (bombarding potential 28 volts).

If the Bragg formula obtained, the maxima in this curve would occur at positions given by $V^{1/2} = n \times 3.06$, where n represents an integer. The wave-length $\lambda(=h/mv)$ expressed in volts V (bombarding potential) is given by $\lambda = (150/V)^{1/2}$ Å, and when this expression for λ is written into the Bragg formula we obtain

$$V^{1/2} = n \frac{(150)^{1/2}}{2d \cos \theta}$$

which reduces to $V^{1/2} = n \times 3.06$ for $d = 2.03$ Å and $\theta = 10$ degrees. The positions which the maxima should then occupy are indicated by arrows in figure 3.

It is evident that there is a simple correlation between the observed and calculated positions of the maxima, but whether the maximum observed at $V^{1/2} = 8.0$ is the third of the series or only the second is not yet certain.

The more general form of the Bragg formula is

$$n\lambda = 2d(\mu^2 - \sin^2\theta)^{1/2}$$

where μ represents the refractive index of the crystal. Writing in $(150/V)^{1/2}$ for λ and solving for μ one obtains

$$\mu = \left[\frac{150\, n^2}{4Vd^2} + \sin^2\theta\right]^{1/2}.$$

In the table below we give values of μ corresponding to the two possible assignments of orders.

TABLE 1

	FIRST ASSIGNMENT		SECOND ASSIGNMENT	
$V^{1/2}$	n	μ	n	μ
[5.3]	1	[0.60]	2	[1.15]
8.0	2	0.77	3	1.14
11.4	3	0.81	4	1.07
14.7	4	0.84	5	1.04
18.1	5	0.85	6	1.02
21.2	6	0.87	7	1.01
24.2	7	0.89	8	1.01

Further observations at other angles of incidence will, we believe, indicate whether the first or the second of these assignments is the correct one, and whether or not the diffraction phenomena can be adequately accounted for by writing an index of refraction into the Bragg formula.

The widths of the peaks shown in figure 3 are determined presumably by the rate of extinction of the equivalent electron radiation in the crystal. It should be possible to calculate coefficients of extinction for electrons of different speeds from such data. In a similar manner it is possible to calculate from the widths of the spurs shown in figure 2 a lower limit to the mean size of facet on the surface of the crystal. These calculations will be carried out as soon as precise data are available.

Several diffraction beams, as distinguished from reflection beams, have so far been observed in the present investigation. It may be shown that the wave-lengths of such beams will satisfy the plane grating formula

$$n\lambda = D(\sin\theta_2 - \sin\theta_1)$$

with respect to the atomic plane grating lying parallel to the surface of the crystal, no matter what value the index of refraction of the crystal may have. This is the formula used in calculating wave-lengths in our previous experiments, and it is used now to calculate the wave-lengths of two diffraction beams for which the data are exceptionally precise. The calculated wave-lengths are in excellent agreement with the theoretical values of h/mv as shown in the accompanying table.

TABLE 2

D = grating constant = 2.15Å;
V = bombarding potential;
θ_1 = angle of incidence;
θ_2 = angle of diffraction (angle between diffraction beam and normal to crystal face, the sign being chosen so that $\theta_1 + \theta_2$ represents the angle between incident beam and diffraction beam);
n = order of beam;
λ (obs.) = $D(\sin\theta_2 - \sin\theta_1)$
λ (cal.) = $h/mv = (150/V)^{1/2}$Å.

V (volts)	θ_1	θ_2	n	λ(obs.)	λ(cal.)	$\frac{\lambda(\text{obs.})}{\lambda(\text{cal.})} - 1$
165	0.0	+62.8	+2	0.956 Å	0.953 Å	+0.003
130	44.5	+11.9	−1	1.064	1.074	−0.01

Our present apparatus, regarded as a spectrometer, is superior to the one employed in our earlier experiments. The positions of beams can be determined with an uncertainty of less than half a degree of arc, and as a consequence the values of observed wave-length given above should be in error by not more than about one per cent. The data obtained in our previous experiments yielded values of observed wave-length which, in a few cases, differed from the calculated values by more than fifteen

per cent (loc. cit., Fig. 17). That we were justified in attributing these large discrepancies to instrumental error seems now quite certain.

It is interesting to note that the first of the diffraction beams for which data are given above is one that was observed under similar conditions (primary beam incident normally) with our first and less precise apparatus. The values found for the critical potential and position of the beam in the earlier experiments were $V = 160$ volts and $\Theta_2 = 60$ degrees.

[1] Eckart, *Proc. Nat. Acad. Sci.*, **13**, 460 (1927).

THE LIMITS OF ACCURACY IN PHYSICAL MEASUREMENTS

By Arthur Edward Ruark

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1. *Heisenberg's Uncertainty Principle and the Motion of Free Particles.*—Heisenberg[1] has called attention to an important feature of our physical measurements. If we determine the value of a coördinate q for a specified value of the time, or possibly of some other parameter, the conjugate momentum p is altered during the measurement. Conversely, if we determine p, then q is changed by the process of measurement. In discussing these alterations, we shall neglect errors caused by the imperfections of the observer. In a measurement of q, let Δq be the uncertainty introduced by the finite "q-resolving power" of the apparatus, and Δp the uncertainty of the conjugate momentum at the same instant. According to Heisenberg,

$$\Delta q \cdot \Delta p \sim h. \qquad (1)$$

Using the concepts of the probability interpretation of quantum mechanics, Darwin[2] justified this relation for certain general types of dynamical systems.[3]

The uncertainty discussed by Heisenberg, due to modification of the measured object by the measuring device, is quite distinct from that ordinarily considered, which arises from the dimensions and imperfections of the measuring device and the observer. It is present even if the observer obtains what we may call "ideal performance" from his apparatus. To illustrate what is meant, we might say that "ideal performance" is attained in a length measurement with a microscope if the precision is of the order of the wave-length of the light employed. To sum up, the content of equation (1) may be restated as follows:

If the coördinate q is measured by an apparatus giving rise to an uncertainty Δq, then p is modified by an amount Δp, such that $\Delta q \cdot \Delta p \sim h$; and a similar statement obtained by interchanging p and q is also true.

It appeared to the author that it should be possible to obtain a device which would determine a dynamical quantity by the use of a trigger, or shutter, without spoiling the system for the observation of the conjugate magnitude. This view was expressed in the program of the December, 1927, meeting of the American Physical Society. Since that time[4] it was realized that the end sought for is unattainable, if the probability interpretation of quantum mechanics is correct. The experiment which was suggested is this: Consider two slits a great distance, d, apart, equipped with movable shutters. Let the first slit open for an interval τ, at time t_1, and let a freely moving particle of unit mass pass through. Let the second slit open for an interval τ, at time t_2. Suppose the particle moves at such a rate that it passes the second slit also. The question is, what can be said about the values of the coördinate x and the momentum p_x of the particle at time t_1? In principle, p_x can be determined with any accuracy we please; for both d and $t_2 - t_1$ can be determined very precisely. (In the next section, we shall see that these very accurate "thought-measurements" cannot be carried out in practice.) Suppose the measured value of p_x is $v \pm \Delta v$. The position at time t_1 is known with the precision $v\tau = \Delta x$, and it is conceivable that $\Delta x \cdot \Delta v_x$ could be small compared with h, if τ and Δv are sufficiently minute. This is fallacious. The velocity of the particle changes when it passes the first slit, for it may be considered as a group of waves and the frequency of each harmonic train in the group is changed by the modulation due to the shutter. This involves a change of energy, that is, a modified velocity. The effect is safely below present-day limits of error in observation. An explanation of frequency changes due to modulation was given by Breit, Ruark and Brickwedde[5] in terms of both classical theory and the older quantum theory. Equation (2) below, taken from their paper, applies to the present example, but we shall use another illustration for the sake of clarity, namely, a quantum passing through a "shutter" which modulates the electric vector sinusoidally. (For example, the shutter may consist of two Nicol prisms, one of which rotates about its axis with frequency N.) We wish to describe the results of this modulation in terms of wave mechanics. The Schrödinger function Ψ for a quantum obeys an equation of the same form as that for plane electromagnetic waves.[6] While so simple a representation of the quantum is perhaps incomplete,[7] it seems reasonable to say that a phenomenon described in classical theory as a modulation of the electromagnetic potentials corresponds in the new theory to a modulation of Ψ. To discuss completely the effect of modulation we must solve the wave equation for the quantum and the shutter;

but we can check equation (1), by using our everyday conceptions, as follows: We wish to know the momentum and position of the quantum at an instant t_1 during a specified opening of the shutter. In passing the shutter, the frequency of the quantum changes by $\pm N$. The final frequency is measured with a spectroscope. We cannot tell whether the frequency has increased or decreased, so the uncertainty of the initial frequency is N, and that of the momentum, hN/c. The position at time t_1 is known only within the limits $\pm c/N$, so that (1) is satisfied.

The modulation of the wave group of a particle passing a sectored disc is described by

$$\cos(2\pi\nu t - \epsilon)\,\Sigma a_n e^{2\pi i n N t} = \frac{1}{2}\,\Sigma a_n \left\{e^{i[2\pi(\nu + nN)t - \epsilon]} + e^{-i[2\pi(\nu - nN)t - \epsilon]}\right\} \tag{2}$$

which states that a periodic amplitude change of frequency N produces the frequencies $\nu \pm nN$, with $n = 0, 1, 2, \ldots$.

It is interesting to see how closely we can approach the situation described by (1) with present-day methods and apparatus. So far as the author can find, the experiments in which $\Delta q \cdot \Delta p$ has been pushed to the lowest values yet attained are of the type described above. Lawrence and Beams[8] constructed an arrangement of Kerr cells, which transmits light flashes having a duration of 10^{-10} sec. If such light segments, 3 cm. long, having the wave-length 5000 Å, were allowed to pass into a spectroscope of high resolving power, we should see two spectrum lines with the frequency difference 10^{10} sec.$^{-1}$. If the spectroscope separates wave-lengths 10^{-2} Å apart in this region, it can detect a frequency difference of 10^{9} sec.$^{-1}$. Since this is ten times smaller than the uncertainty introduced by modulation, a study of the displaced lines is at the same time a test of equation (1). Rupp[9] used a single Kerr cell to study the frequency shift due to modulation, with a thallium resonance lamp as a source and a second thallium resonance bulb as a "spectroscope" for studying the modulated light. He states that the results agree with the classical theory.

The uncertainty principle is a statement about the information which can be gained from a single experiment. In the illustration of a light beam modulated by a rotating Nicol, suppose we measure the frequency of only one transmitted quantum, obtaining the number f_1. Since we do not know whether the frequency increased or decreased in passing the modulating device, we cannot tell whether the original frequency was $f_1 + N$ or $f_1 - N$. Suppose now we measure the frequency of a second quantum, with the result $f_2 = f_1 - 2N$. The classical theory tells us the original frequency of both quanta was $(f_1 + f_2)/2$. This illustrates a procedure tacitly but generally used by which we obtain more information from a

number of *precisely similar* experiments than we can from only one experiment. The situation can be analyzed, using the concept of the "pure case" introduced by Weyl[10] and von Neumann.[11] For example, an aggregation of quanta, all with the same frequency, polarization and momentum, constitutes a pure case. All observable properties of one quantum are the same as those of any other in the beam. In the interpretation of the above experiment we assume that the quanta constituted a pure case initially. Modulation splits them into a mixture of pure cases. At this point, we put our trust in the ability of classical theory to give us detailed knowledge of the possible alterations, and thus determine the properties of the original pure case.

2. *The Limits of Accuracy in Physical Measurement.*—Equation (1) deals with changes in the q's and p's of a system, brought about by the observing instrument. We now point out another aspect of the situation, with an interesting conclusion as to the accuracy with which a *single* dynamical quantity can be measured. If the q's and p's of the measuring device, B, are of the same order as those of the measured object, A, then the changes in B caused by A must be considered. The coupled system $A + B$ must be treated as a whole, and the interpretation of a measurement consists in answering the question, what can we say about a coördinate of A when we have determined a coördinate of B with our gross instruments? An example is the measurement of the position of an electron initially at rest, by allowing it to scatter a light quantum of wave-length λ_0. If we attempt to measure the position very accurately by reducing λ_0, a limit is imposed by the increase in wave-length during the scattering process. For an electron, this increase is of the order h/mc, and this is the order of magnitude of the smallest length which can be resolved in such an experiment. This length is large compared with the radius of a Lorentz electron, computed classically on the assumption that the entire mass is electromagnetic. The radius is given by the formula $2e^2/3mc^2$. If we experiment with a body of greater mass M—a proton, for example—the Compton shift is smaller in the ratio m/M, but the radius of the particle is smaller in the same ratio, assuming its structure to be the same as that of the electron. Therefore, in measurements of this kind the ratio of the "radius" of the particle to the smallest resolvable length is

$$\frac{r}{\lambda} = \frac{2e^2/3mc^2}{h/mc} \cong \frac{e^2}{hc}. \qquad (3)$$

Aside from a factor 2π this is identical with Sommerfeld's fine-structure constant $2\pi e^2/hc$. Both the classical and the quantum theories are used in deriving (3). It is perhaps more satisfactory to consider r in (3) as an effective radius obtained from scattering experiments and to think of

λ as obtained from experiments on the Compton shift, regardless of any theory.

This result indicates a definite limitation which affects any attempt to study the structure of an individual electron by the use of light quanta. To be sure, when light is scattered by an electron of high velocity, the wave-length of the scattered quantum may be less than that of the incident quantum. However, this offers only a partial avenue of escape. The longitudinal dimension of an electron is presumably decreased because of the Fitzgerald-Lorentz contraction and a simple calculation shows that the ratio of this dimension to the scattered wave-length is always of the order of magnitude specified by (3). The transverse dimensions are not affected and, therefore, they should be more easily studied, in principle at least, if not in practice.

The question now arises, is there a similar restriction on the delicacy of length measurements when the exploring instrument is a swiftly moving particle? Since our final measurements must be made with gross apparatus, we are justified in using the equations of energy and momentum. The wave-length of the de Broglie waves for a particle is h/p, where p is the momentum *after* collision. This wave-length determines the smallest length interval detectable by such a collision. The question is—can we make h/p as small as we please by proper choice of the initial velocities? If the particle to be studied is moving rapidly then it can transfer energy and momentum to the particle used as a measuring device, reducing the wave-length of its de Broglie waves. This shows the utility of experiments in which alpha-particles impinge on rapidly moving atoms, as, for example, the ions in a positive ray-beam. However, more interest attaches to experiments in which the bombarded atoms of mass M are initially at rest. A detailed study of collisions in which these atoms are struck by particles of mass m moving with velocity $\beta_i c$ leads to such algebraic complexity that it is not useful. However, much progress can be made by studying representative cases. After the collision let the particle m move with velocity $\beta_f c$ making an angle Θ with its initial direction of motion and let particle M move with velocity Bc at an angle Φ with the initial velocity of m. Writing the equations of momentum and energy, and eliminating B and Φ, we have:

$$\beta_f = \frac{\nu m\beta_i \cos\Theta \pm \mu\sqrt{(M^2 - m^2)\beta_i^2 + m^2\beta_i^2\cos^2\Theta}}{\mu^2 + m^2\beta_i^2\cos^2\Theta}. \qquad (4)$$

In this expression $\mu = M + m\sqrt{1-\beta_i^2}$, and $\nu = M\sqrt{1-\beta_i^2} + m$, so that μ approaches M and ν approaches m when β_i approaches one.

The wave-length h/p can be evaluated for any interesting case, remembering that $p = m\beta_f c/\sqrt{1-\beta_f^2}$. For example, let ν be very large compared with μ; then when β_i approaches one the particle m can be

deflected only through a small angle. If Θ has the maximum value which it can attain, then

$$h/p \longrightarrow (h/mc)(M/m).$$

Again if $M = m$, $\nu = \mu$, and h/p approaches h/mc multiplied by a function of Θ which is of the order of unity for deflections of reasonable magnitude. Further, if ν is very small compared with μ and β_i approaches 1, h/p approaches $(h/mc)(m/M)$ multiplied by a function of Θ having the properties mentioned in the previous case.

These results indicate a definite limit on the accuracy of measurement with the arrangements described. So far we have spoken only of length measurements. Similar restrictions affect our measurements of time and also of momentum variables. These variables usually involve velocities, and measurements of velocity involve measurements of length, so that any restriction on the accuracy of length measurement will also affect the determination of velocities, accelerations and masses.

It is well to emphasize that the limitations described in this section apply to single experiments. Nothing has been said about information on electronic or protonic structure derived from the statistical results of scattering experiments. We are faced with a situation which is strange but not illogical, namely—it seems possible that statistical results give us more information than individual experiments. In interpreting such results, however, it is customary to *assume that the structure of the elementary particles is definite and quite independent of past history or external conditions*. Since this assumption is questionable, we cannot be sure that statistical results tell us anything about the structure of an individual particle which we single out for study. [4]

The results of this paper do not cripple the program of applying causal law and continuous analysis to sub-electronic problems; but in so far as the assumptions used are valid in this domain they deprive such a program of experimental support—the sine qua non of physics—and throw the problem into the realm of speculation.

Much of this material originated in discussions with Dr. Harold C. Urey, whom I wish to thank for his generous coöperation. I am also indebted to Dr. J. J. Weigle, Dr. N. P. Rashevsky, and Dr. J. C. Slater for extremely helpful comments.

[1] *Z. Physik*, **43**, 172 (1927).

[2] *Proc. Roy. Soc.*, **A117**, 258 (1927).

[3] Bohr showed that for the hydrogen atom the right side of (1) should be replaced by nh, n being the total quantum number. *Transactions of the Volta Centenary Congress*, Como, 1927. I have not had the opportunity to see this publication.

[4] See program of the February, 1928, meeting.

[5] *Phil. Mag.*, **3**, 1306 (1927).

[6] Epstein, *Proc. Nat. Acad. Sci.*, **13**, 94 (1927).

[7] Ruark and Urey, *Proc. Nat. Acad. Sci.*, **13**, 763 (1927).
[8] *Ibid.*, **13**, 207 (1927).
[9] *Physik. Z.*, **18**, 901 (1927).
[10] *Z. Physik*, **46**, 1 (1927).
[11] Mentioned in Weyl's article.

A CRITICAL EXPERIMENT ON THE STATISTICAL INTERPRETATION OF QUANTUM MECHANICS

By Arthur Edward Ruark

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Consider a dynamical system with a single coördinate q, and energy E, and let Ψ represent the Schrödinger wave function of this system.

It is commonly stated that the function

$$w(q_0, E_n)dq_0 \equiv \Psi(q_0, E_n)\ \Psi^*(q_0, E_n)dq_0$$

is a measure of the probability that q shall lie between q_0 and $q_0 + dq_0$ when the energy E takes the quantized value E_n. The absolute value of the Schrödinger Ψ-function appearing in this relation is called the "probability amplitude." More generally, it is postulated in the statistical interpretation of the quantum dynamics of such a system, that for every pair of dynamical quantities, x, y, there exists a function

$$\varphi(a, b;\ x, y),$$

of such a kind that when y takes the value b, the probability for x to lie between a and $a + da$ is

$$w(a,b;\ x,y)da \equiv \varphi(a,b;\ x,y) \cdot \varphi^*(a,b;\ x,y)da.$$

At present, the meaning of the word "probability" used in these definitions is controversial. Following Born,[1] one school of thought has advocated the view that the probability functions refer to the average behavior of a great number of similar systems, and that $\Psi\Psi^*dq_0$ measures the fraction of the systems for which q lies between q_0 and $q_0 + dq_0$. Again, the velocity distribution of a large number of electrons having the same definite position, $q = q_1$, will be such that $w(v_1, q_1;\ v, q)dv_1$ is proportional to the fraction having velocities between v_1 and $v_1 + dv_1$. Darwin's[2] attitude is representative of another view, based on Heisenberg's uncertainty relation.[3] Darwin states that each electron in a group of the kind considered above has the whole velocity distribution and should not

be considered as possessing a definite velocity. This statement is not unreasonable if we interpret it as meaning that experiments to determine the velocity are necessarily very inaccurate, when the coördinate q is known with great precision. Similarly, it is assumed that a single atom can exist in several different quantized states at once. In terms of the older quantum theory, this is nonsense, but Schrödinger's theory removes the difficulty. In wave mechanics, we visualize the idea that an atom has several different energies by saying that it has several different frequencies—that several of its modes of stationary vibration are present simultaneously.

The following experiment may serve to decide between these two views. Consider a radioactive nucleus having several high-lying energy levels, such as RaB or RaC.[4] If a single nucleus can possess two or more stationary modes of vibration simultaneously, then it seems probable, though not certain, that it can emit two or more gamma-ray quanta before exhausting the vibration amplitudes corresponding to the high energy levels. Suppose we let the gamma-rays from RaB and RaC fall on a crystal arranged as in the measurements of Rutherford and Andrade.[5] Instead of receiving the diffracted quanta on a photographic plate, we let them fall into small point counters, spaced in such a way that each counter intercepts only rays belonging to a single spectrum line. The point counters may actuate any convenient type of recording mechanism. The number of cases in which two (or more) counters record a gamma-ray quantum can be checked against the number of multiple counts which might be expected as a result of fortuitous coincidence in the breakdown of two separate atoms.

Kovarik[6] has performed counting experiments which indicate that only one gamma-ray is emitted by each decomposing atom of RaB or RaC. The discrepancy between the number of gamma-rays counted and the number of atoms decomposing is about 2%, which may be due to experimental error, according to Kovarik. This shows that double emissions of the kind described above occur but seldom, if at all. Measurements by Ellis and Wooster[7] furnish strong support of Kovarik's results.

Again, if double emissions occur, the conservation of energy is only statistical. Any experiment which indicates that energy and momentum are conserved in each elementary process, such as the experiment of A. H. Compton and Simon,[8] speaks against such a view. Of course, if it is proved that double emissions do not exist, this would not *demonstrate* that only one stationary vibration is excited. A comparison with the behavior of a violin string carrying several harmonics, and giving beat notes with another string, makes the inference very strong that such is the case; but it is an unwarranted extrapolation to carry over this result of macroscopic mechanics into the field of atomic phenomena. Supposing

that several modes of vibration are excited at once, we have no experience available to aid us in setting up an expression for the probability of a double emission from the nucleus.

In conclusion, the experiment suggested above is critical in one direction only, and previous experiments point strongly to the conclusion that the principles of energy and momentum are valid in each atomic process. Such experiments are a sheet anchor of faith when we seek to apply exact laws to occurrences within the nucleus.

[1] *Z. Physik*, **38**, 803 (1926) and **40**, 167 (1926).

[2] *Proc. Roy. Soc.*, **A117**, 258 (1927).

[3] *Z. Physik*, **43**, 172 (1927). See also the preceding paper.

[4] Ellis and Skinner, *Proc. Roy. Soc.*, **A105**, pp. 165 and 185 (1924).

[5] *Phil. Mag.*, **27**, 854 and **28**, 263 (1914).

[6] *Phys. Rev.*, **13**, 272 (1919); **14**, 179 (1919); *Proc. Nat. Acad. Sci.*, **6**, 105 (1920); *Phys. Rev.*, **23**, 559 (1924).

[7] *Phil. Mag.*, **50**, 521 (1925).

[8] *Phys. Rev.*, **26**, 290 (1925).

DIRECT AND INDIRECT CHARACTERISTIC X-RAYS: THEIR RATIO AS A FUNCTION OF CATHODE-RAY ENERGY

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I. *Introduction.*—In the June, 1927, issue of these PROCEEDINGS an account was given of some preliminary experiments on the ratio of the intensities of characteristic x-rays produced by the two processes that occur in any ordinary x-ray target and have been called the direct and indirect processes. The direct process may be defined as the ejection of K electrons from atoms by impact of the cathode rays on those atoms and their resulting reorganization; the indirect process is the ejection of K electrons by photo-electric effect of continuous-spectrum x-rays excited by cathode rays in other atoms. Two questions arise here: one is whether these processes both occur to any noticeable extent; and the other is on the nature of the direct process, whether it is an action of the cathode rays upon the K electrons themselves, or production of continuous-spectrum x-rays and re-absorption within the same atom in which they are produced. The first of these questions is relatively easy to answer experimentally and forms the main question of this research. The second cannot be answered quite so definitely, but there is some evidence on it which will be discussed in the following paper.

The paper referred to above described experiments of two types. One was an analysis of the rays emerging at different angles from the surface of the target, and gave a qualitative conclusion that both processes, direct and indirect, must occur in notable amounts. The other experiment was more quantitative and was based on the use of a block of cadmium covered with a thin sheet of silver, the general principle being that all the direct rays must be produced in the silver, whereas a calculable fraction of the indirect rays must come from the cadmium. From the ratio of the intensity of the silver Kα line to that of cadmium an estimate was made of the ratio of the direct rays to the total indirect. In the present experiments this block-and-film method was used and the work was extended to voltages from 35 to 80 kv., using, as before, direct current at very steady voltage. At the same time additional precautions against error were introduced, and the apparatus was almost completely reconstructed, so that the present work not only covers a wider range than the first, and with greater accuracy, but also constitutes practically an independent research.

II. *Apparatus.*—The apparatus used for these experiments was a special x-ray tube with removable anode, permitting changes in the silver films, and a spectrometer of the Bragg type for measurements of the x-rays by ionization. As the general principles of such apparatus are well known, it will not be described in detail here except for such points as refer specifically to the prevention of errors in this problem.

The first feature of this type is the elimination of some defects encountered in the previous work at the source of the rays. The silver films used then were either sheets of rolled silver foil or films plated on thin sheets of graphite. In either case, warping due to the concentration of heat at the focus of the cathode rays caused the films to move away from the surface of the cadmium. This gave an opportunity for the primary continuous-spectrum rays produced in the silver to spread somewhat before striking the cadmium, and, therefore, to produce their indirect characteristic rays outside the part of the target visible through the slits of the spectrometer. A large part of this loss of rays was compensated by a spreading from other parts of the focus into the visible region, but, of course, such compensation could not be perfect, and special investigation showed that this loss of rays was an unexpectedly large source of error.

The rolled foil had also the disadvantage of a few minute holes; and although it was otherwise very uniform so far as could be told by absorption tests, the absorption coefficients calculated from these tests, as well as their K discontinuity ratio, came out 5 to 10% low, indicating a lack of uniformity on a scale too small for direct measurement. The thickness, by weight and area, was 5.6 microns, whereas by absorption, using Richtmyer's[1] absorption coefficients, it appeared to be 5.4 on the long-wave

side of the K limit and 5.2 in the K-absorption band. This indicates the existence of thin spots, which may let some cathode rays through at such voltages as 80 kv., especially the rays that happen to go unusually straight. Such cathode rays would excite x-rays directly in the cadmium. The silver films plated on graphite are free from this trouble, but they persisted in slowly warping. Consequently, foil was used in all the work to be reported here, and was backed with 40-micron aluminum between it and the cadmium.

To prevent the spreading of the rays with this combination, the surface of the cadmium block was changed to a segment of a cylinder 3.4 cm. in radius, with its axis lying horizontal and perpendicular to the slits. The silver foil was then cut to a ribbon 6 or 7 mm. wide and stretched across the cadmium with a spring to keep it under tension, and the aluminum was not under tension. This arrangement gave close contact everywhere.

An important feature in the work with these targets was the measurement of the rays by a quick ballistic method, previously described,[2] for the use of an electrometer. This resulted in a great saving of time in the running of the tube, without which it would have been impossible to get enough measurements for even a single estimate of the ratio of the silver and cadmium lines before the disintegration of the silver under cathode-ray impact would cause the ribbon to tear.

This disintegration may possibly have been accompanied by some loss of silver by evaporation. The cadmium was water-cooled and the power input was only 4 watts, about half of which missed the ribbon; but the thermal contact of the silver with the cadmium in a high vacuum is not nearly so good as might be expected from experience with such things in air; and the light of the filament made it impossible to be certain that the ribbon was not a dull red heat. It seems more probable, however, since each cathode ray carries enough energy to heat every atom it penetrates above the melting point, that the disintegration is due largely to local heating and recrystallization near the ends of the cathode-ray paths. If so, no allowance need be made for loss by evaporation.

The geometric conditions of this source were: emergence angle of the x-rays used, 90° at the center and nearly enough so everywhere to call its sine unity; inclination of the target surface to the axis of the tube, 33°; probable inclination of the cathode rays to the surface, as they strike it after deflection by the unsymmetrical electrostatic field, about 45° ± 5°.

For reasons explained below, it was necessary to estimate the mean depth of production of the primary rays, using the absorption-limit method.[2] To eliminate rays entering by second-order reflection, Kirkpatrick's method[3] was used, with a copper filter. This correction was minimized by the use of an ionization chamber especially designed to absorb most of the Cd Kα line rays, while discarding by transmission

most of the rays of half that wave-length. For this purpose it was made 29 cm. in inside length, with a thin aluminum window (40 microns). In the further end, covering the inside of the brass end plate, was a sheet of 2 mm. aluminum to suppress any fluorescent rays from the brass. The chamber was carefully tested for air-tightness. It was then set to receive the cadmium line rays, while the tube was run with the cadmium block alone. The chamber was then pumped and filled slowly with methyl bromide, and ionization measurements were taken at intervals to see how much methyl bromide was needed. These measurements agreed excellently with calculations from the atomic absorption coefficient of bromine, 5.14×10^{-21} cm.^{2}, given by Richtmyer's formula.[1] The filling was stopped at 59 cm. pressure, where the fraction of the cadmium-line rays absorbed was 0.963.

To insure against errors due to lack of saturation in the ionization current, the collecting electrode was a large plate running almost the whole length of the chamber, and another plate connected to the walls was set parallel to it on the other side of the rays, the potential difference between them being 90 volts.

III. *Calculations.*—The calculation of the ratio of the observed cadmium rays to the indirect radiation that would occur in a solid silver target, and likewise the calculation of the deduction from the observed silver rays for such indirect radiation as may arise in the film, were made by practically the same method as was used in the previous paper. There is, however, one notable change. The assumption that all the primary continuous-spectrum x-rays originate in the surface is replaced here by the assumption that they originate at a depth equal to the average depth as measured by the absorption limit method. This change is needed because the continuous-spectrum rays coming out towards the surface produce an appreciable fraction of the total indirect radiation. Thus the calculated value for the total indirect radiation is increased, largely in the part coming from the silver. In the former calculations, for 50 kv., the fractions of the total indirect radiation coming from the cadmium and the silver were 0.47 and 0.44, respectively; here they are 0.455 and 0.50.

These new fractions are derived as follows: Let E be the total intensity of α-line rays leaving the target, defined as energy per unit time, per unit solid angle and per electron in the cathode rays. This item, per electron, is unimportant at present, but will be of use in the following paper. Likewise, let E' and E'' be the direct and indirect (or primary and secondary) intensities. Let E''_{Cd} and E''_{Ag} be the indirect rays from the cadmium and silver, respectively; let E''_b be the rays that would come from the block if it were silver; let E''_+ and E''_- be the indirect rays from a solid silver target, from depths greater and less, respectively, than the

mean depth, $\bar{x}$, of production of the continuous spectrum rays. E''_+, E''_- and E''_b are calculated first. Then

$$E'' = E''_+ + E''_-,$$

and

$$E''_{Ag} = E'' - E''_b.$$

E''_{Cd} is then obtained by correcting E''_b for the effect of the aluminum foil and for differences in the properties of cadmium and silver.

With these definitions,

$$E''_+ = \frac{1}{2}\int_{\nu_K}^{\nu_0}\int_0^{\frac{\pi}{2}}\int_0^{\infty} u_\alpha \frac{\nu_\alpha}{\nu} I(V,\nu) e^{-\mu r - \mu_\alpha r\cos\psi - \mu_\alpha \bar{x}} \sin\psi\, dr d\psi d\nu.$$

Here ν_0 is the high-frequency limit eV/h, ν_K the K-absorption-edge frequency, ν_α that of the α line, the μ's are absorption coefficients, u_α the fraction of the absorbed quanta that reappear as α-line quanta, $I(V, \nu)$ the intensity per unit frequency interval in the continuous spectrum, and r and ψ are the radius and colatitude of a spherical coördinate system centered at a depth $\bar{x}$. It is assumed here, as in the previous paper, that I is independent of ψ.

E''_b is derived from a similar integral changing only the lower limit for r, from 0 to $(x_1 - \bar{x})$ sec ψ, where x_1 and $\bar{x}$ are the film thickness and mean depth of production of primary rays, respectively. For x_1, the value 5.40 microns was used. For $\bar{x}$, at voltages 35, 50, 65 and 80 kv., the values used were 0.70, 1.25, 1.75 and 2.30 microns, respectively, these values being calculated from spectra of the cadmium block alone. (These spectra, being on a scale small enough to include the peaks of the lines, do not give $\bar{x}$ with great accuracy, but with enough for present needs.)

For E''_-, the integrand is the same, but the limits are: for ψ, $\frac{\pi}{2}$ to π; for r, 0 to $-\bar{x}$ sec ψ.

To simplify the integration, $I(V, \nu)$ is approximated as $K(\nu'_0 - \nu)$, or $K\nu_K(s'_0 - s)$, where K is a constant, and s'_0 exceeds s by 0.06, 0.09, 0.13 or 0.18 at 35, 50, 65 and 80 kv., respectively. These data are estimated from isochromats of Mo plotted by Webster and Hennings[2].

The expressions then integrate to the following:

$$E''_+ = Le^{-\mu_\alpha \bar{x}} S(V, 0)$$

$$E''_b = Le^{-\mu_\alpha x_1} S(V, x_1 - \bar{x})$$

$$E''_- = LT(V, \bar{x})$$

where $L = \frac{1}{2} K u_\alpha \nu_\alpha \nu_K$

$$S(V, x) = \int_1^{s_0} \left(\frac{s_0'}{s} - 1\right) \frac{\mu}{\mu_\alpha} \left\{ e^{+\mu_\alpha x} Ei(-(\mu + \mu_\alpha)x) - Ei(-\mu x) \right\} ds$$

and

$$T(V, x) = \int_1^{s_0} \left(\frac{s_0'}{s} - 1\right) \frac{\mu}{\mu_\alpha} \left\{ e^{-\mu_\alpha x} \left[Ei(-(\mu - \mu_\alpha)x) - \log \left| \left(1 - \frac{\mu_\alpha}{\mu}\right) \right| \right] - Ei(-\mu x) \right\} ds.$$

In $S(V, 0)$, the $\{\quad\}$ reduces to $\log\left(1 + \frac{\mu_\alpha}{\mu}\right)$, and by the use of series all these expressions could presumably be integrated. Practically, however, Simpson's rule does the work more readily, 6 panels giving ample accuracy. For this, μ_α and μ were taken as 139 and $(651s^{-3} + 10)$ cm.$^{-1}$, respectively, these being derived from Richtmyer's formula, with the density 10.5 gm./cm.^{3}; in cadmium, these linear absorption coefficients are almost exactly the same as in silver, and the ratio, which is the only function of them actually affecting the result, is even more exactly the same.

To get E''_{Cd} from E''_b, the first step is to subtract the part of the integral due to the frequency range from the K-absorption edge of silver to that of cadmium. This correction is E''_Δ, tabulated below. Next comes a factor G, for the aluminum, involving a weighted average of losses by absorption for various directions and frequencies, none of them large enough to make serious errors if not averaged very accurately. The next factor, H, is estimated likewise for the difference in the absorption of CdKα rays from that of AgKα in either cadmium or silver. Then, there is the spectrometer sensitivity factor, J, due to differences in properties of these two rays in glass, air, calcite, aluminum and methyl bromide. This was estimated for each of these substances, assuming that the calcite factor is unity, and was checked within 2% by an overall estimate from the assumed formula for $I(V, \nu)$ and the slope of the observed graph of the continuous spectrum.

The results of all these calculations are shown in table 1.

TABLE 1

V	35	50	65	80 KV.
E''_+/L	0.0710	0.341	0.723	1.176
E''_-/L	0.0102	0.065	0.161	0.300
E''_b/L	0.0348	0.203	0.473	0.828
E''_Δ/L	0.0073	0.0197	0.0341	0.0500
GHJ	1.005	1.01	1.015	1.02
$f_{Ag} = E_{Ag}/E''$	0.572	0.500	0.465	0.439
$f_{Cd} = E''_{Cd}/E''$	0.340	0.455	0.504	0.538

IV. *Spectra.*—Some of the spectra to which these ratios were applied

are shown in figures 1–4. The spectra of the bare cadmium block, shown in circles, were plotted first, using tube currents large enough for as good accuracy as could be obtained, and taking many measurements. Then

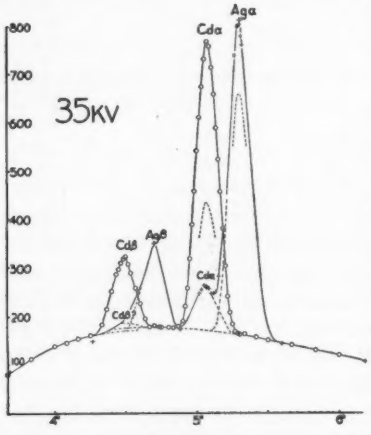

FIGURE 1

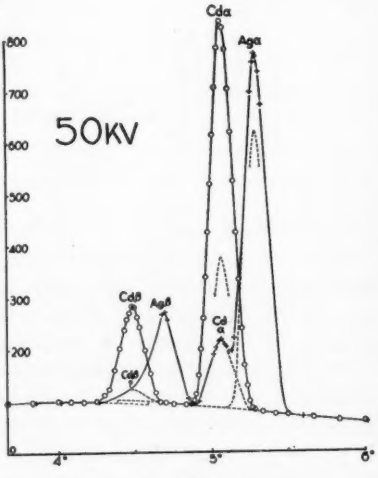

FIGURE 2

the silver films were put on, and enough points were taken to fix the peaks and to repeat several times at each peak, and to determine a constant factor that would fit their continuous

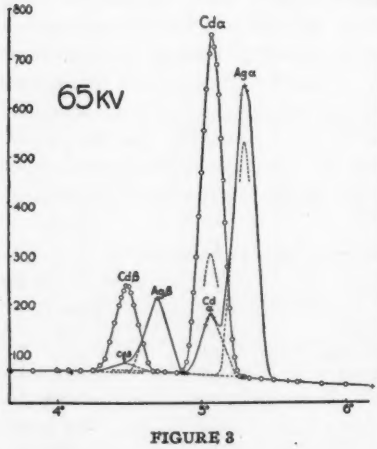

FIGURE 3

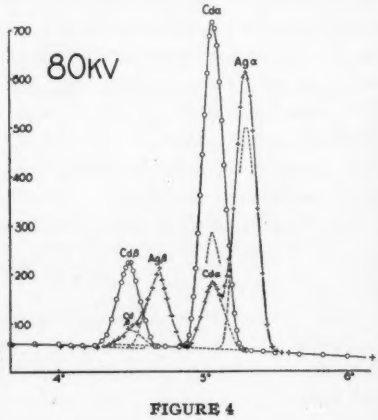

FIGURE 4

spectra to those of the cadmium. This procedure gives a degree of accuracy in the deductions for continuous spectrum intensity such as could

not be obtained otherwise, and also shows that an α-doublet peak is not wide enough with the slit widths used to cause the base of either peak to reach the optimum angle for the other. On this point, additional assurance is given by the regularity with which the Cdα peaks exhibit all the features of the theoretical form of an unresolved doublet with a 2 to 1 ratio.

The ordinates here are millimeters deflection of the electrometer, those above 500 being corrected for non-linearity of the scale by amounts up to 1.5%. The abscissas are glancing angles, standardized in each case by calling the optimum angle for cadmium 5°4′. The correction for second order reflection has not been applied in plotting here, but is less than 10% of the continuous spectrum intensity at the lines, even at 80 kv., and almost negligible at 65.

Letting a_{cd} and a_{ag} represent maximum α peak ordinates (after deducting the continuous spectrum), the ratio of direct rays to indirect is

$$P = \frac{E'}{E''} = f_{cd}\frac{a_{ag}}{a_{cd}} - f_{ag}.$$

A check on the location of optimum angles for measurements was obtained from data at corresponding points 1′ or 2′ on the same side of each maximum, giving the same ratio as the maxima.

V. *Results.*—The results of these calculations and measurements, taken in all from 3 films, are shown in figure 5, the values of P being as follows:

TABLE 2

	v	35	50	65	80 kv
From data,	P	1.83	1.89	1.96	1.96
From graph, figure 5,	P	1.83	1.89	1.94	1.97

As predicted in the earlier paper, P does not vary much with voltage, even over a range of voltages causing E'' to vary by a factor of about 18. The values of P given here, however, are considerably lower than the 2.36 found in that work at 50 kv. About four-fifths of this change is due to the elimination of losses of primary rays by spreading, discussed above, the remaining fifth being due to the new assumption about the depth of production of the primary rays.

The sources of error in this work are very numerous. On the experimental side, in 40 pairs of data (a_{ag} and a_{cd}), the mean deviation of P from the values given by figure 5 was almost 3%, with greater differences between pairs from different films than from the same film. On the mathematical side, there are the numerous assumptions entering into the calculation of the theoretical intensity ratios for a silver film on a silver block, and the ten corrections listed above for the differences between silver and cadmium. The fact that nine of these, included in the product GHJ, give a result never differing from unity by over 2%, is quite misleading, for if they had all worked in the same direction, the product

would have differed from unity by over 15% at all voltages. It is difficult to estimate the overall probable error with so many sources for it, but I should certainly place it as high as 10% or perhaps even 20.

In the application of this ratio to problems in the theory of line-spectrum intensities, there are still further uncertainties. It seems highly probable, in view of the influence of the depth of production of the primary rays upon the calculated values for E'', that the extent to which the focal spot of any target has been roughened by recrystallization under cathode-ray impact must have a marked effect on the ratio P for that particular target. The fact is, of course, that except for the study of doublet intensity ratios, any thick-target data must be regarded as provisional, to be used only until they can be replaced by corresponding data from extremely thin targets. The utility of this ratio P is, first, to establish the validity of a method already in use here with thin targets, as described in the earlier paper, and second, to furnish a basis for certain order-of-magnitude estimates, not readily obtained with the thin targets, as discussed in the next paper.

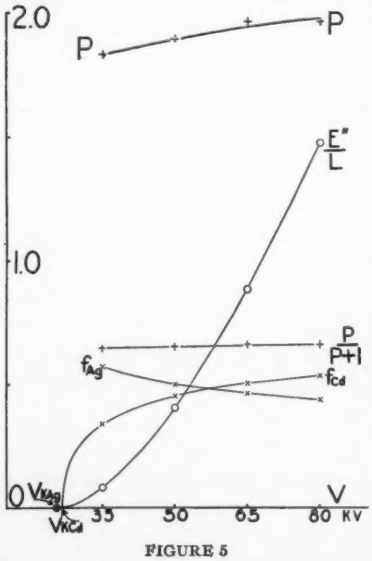

FIGURE 5

VI. *Application to Current Comparisons of Theories and Data on E as a Function of V.*—One immediate application of these results is to tests of theories of line-spectrum intensities as functions of cathode-ray energy, in which the theories have usually been concerned with direct rays only, while the data with which they have been compared have included both direct and indirect together. If the indirect were unimportant, the use of such data would involve no special assumption. As it is, however, the direct radiation is a fraction, $P/(P+1)$, of the whole, and such tests mean nothing unless the behavior of this fraction as a function of voltage is known. Fortunately, from this standpoint, it turns out to be very nearly constant, as shown in figure 5, and current tests, containing an arbitrary intensity unit, are practically valid.

VII. *Summary.*—1. The researches previously outlined, on the ratio of direct characteristic radiation to indirect, have been extended with improved accuracy. The value of this ratio for silver is almost

constant, the data giving 1.83 at 35 kv. (1.375 V_K) and 1.96 at 80 kv. (3.14 V_K), with a probable error of 10 or 20 per cent.

2. This variation is not sufficient to vitiate current comparisons of observed line intensities with theories.

In conclusion, it gives me great pleasure to express my heartiest thanks to my associates in this laboratory for very valuable help in this work, and especially to Mr. B. G. Stuart on the mechanical side of it and Mr. W. W. Hansen on the mathematical.

[1] F. K. Richtmyer, *Physic. Rev.*, **27**, 1 (1926).

[2] D. L. Webster and A. E. Hennings, *Ibid.*, **21**, 301 (1923).

[3] Paul Kirkpatrick, *Ibid.*, **22**, 37 (1923).

K-ELECTRON IONIZATION BY DIRECT IMPACT OF CATHODE RAYS

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I. *Introduction.*—In the preceding paper, the question was raised whether the direct process of K-electron ionization by cathode rays was usually a process of electrostatic repulsion or whether it might be more often a sort of internal photoelectric effect, like the indirect process except that the absorption of the primary rays is assumed to occur within the same atom in which they are produced. The former of these processes, which we shall call for brevity the strictly direct process, is what one would have most naturally expected a few years ago; the latter, semi-direct as we shall call it, is strongly suggested by Auger's[1] discovery of just such a process in the production of secondary photoelectrons, differing only in that here the radiation absorbed belongs to the continuous spectrum rather than the lines. The problem here is to collect evidence as to which of these processes occurs the more often, some of this evidence also being of interest for other problems.

II. *The Intensity Ratio of Line and Continuous Spectra.*—The evidence considered here is based on calculations of intensities and intensity ratios, using formulas derived from the same basic assumptions as those of the preceding paper, and also using the values of the ratio P (direct-to-indirect intensity ratio) found there. It is, therefore, desirable, first, to check these formulas by comparison with experiment, on a quantity on which data can readily be obtained. The quantity chosen for this purpose is the ratio of the indirect Kα-line rays of silver to its continuous-spectrum rays of the same wave-length, defined more exactly as the ratio of the *area* A''

of the indirect-ray peak to the *ordinate* C of the continuous spectrum under it. This ratio is equal to the width of a block of the continuous spectrum, centered at the line and containing integrated intensity equal to the intensity of the line. As such, it should be independent of all questions of resolving power, sensitivity function, etc.

This independence was first checked for the corresponding ratio A/C, for the total α-line area, for cadmium, with changes of slit widths, length of chamber and pressure of methyl bromide. It held good within limits of error, a few per cent, provided that the tube voltage was constant and that the rays reflected in the second order were deducted from C. For a high degree of accuracy, the correction to C for rays scattered diffusely by the crystal should be thoroughly studied. Here, A/C for Cd Kα is raised 2% for this effect, for the other lines 1% or less.

To find A''/C from the data at hand, where the composite spectra contain very few readings on the sides of the peaks, it was first established with the cadmium alone that, keeping the slit widths constant, the ratio of area to peak ordinate (A/a) was independent of voltage. This held good to 1%, a, of course, being measured from the continuous spectrum to the top of the peak. A'', then, can safely be found from its peak ordinate a'' and this ratio. a'' itself, of course, comes from the cadmium peaks in the composite spectra, as $a'' = a_{cd}/f_{cd}$.

A''/C as given by experiment is, therefore,

$$\left(\frac{A''}{C}\right)_{\text{obs.}} = \frac{a_{cd}}{f_{cd}}\left(\frac{A}{a}\right) \div C.$$

As predicted, theoretically, it should be

$$\left(\frac{A''}{C}\right)_{\text{theor.}} = \frac{1}{2}u_\alpha \tan\theta_\alpha \frac{E''/L}{(s_0' - s_\alpha)\exp(-\mu_\alpha \bar{x})}.$$

The notation and numerical values of quantities used here are all as in the preceding paper, with the addition of Θ_α, the α-line glancing angle, and Balderston's[2] value of 0.625 for u_α.

The following table gives values of these quantities and incidentally also those of A/C for cadmium for the α and $\beta\gamma$ peaks, using appropriate values of C. The units of A/C are minutes of arc.

TABLE 1

V	35	50	65	80 KV.
$(A''/C)_{\text{theor.}}$	14.0	33.8	48.7	60.6
$(A''/C)_{\text{obs.}}$	17.6	41	52	68
$(A/C)_{\text{Cd}}$	38	98	138	175
$(A/C)_{\text{Cd}}$	9.5	21	29	36

The theoretical values here are all low but of the right order of magni-

tude. In the use of the same basic assumptions, to be made below, u_a will cancel, and C will not enter into the equations. If, therefore, u_a and C should happen to be the chief sources of error here, they will not affect the later conclusions. Otherwise, the values of PE''/L, which will enter the later equations, are probably in error in much the same ratio by which these values of $(A''/C)_{\text{theor.}}$ differ from $(A''/C)_{\text{expt.}}$.

III. *The Probability of Direct K-Electron Ionization, Relative to Its Continuous-Spectrum Equivalent.*—This ratio is more accurately calculable than the absolute probability of direct K-electron ionization, and will be called here the relative probability. Exactly defined, it is the ratio of the probability that a cathode ray will eject a K electron directly to the probability that the cathode ray will cause emission of a continuous-spectrum quantum having energy great enough to eject a K electron if absorbed.

The value of this relative probability is readily found to be

$$Q = \frac{1}{2}\,\frac{PE''/L}{1 - s_0 + s_0' \log s_0}\, e^{+\mu_a \bar{x}}.$$

Numerically, using the calculated E''/L and the data for P from the tables in the preceding paper, this gives for silver,

TABLE 2

v	35	50	65	80 kv.
Q	0.915	0.92	0.925	0.90

In other words, Q is practically constant at 0.9 (the probable error being 10% or more), even though the value of either of the probabilities compared by it changes by a factor of 19 in the range of voltages covered.

In a thick target at a high voltage, most cathode rays presumably go through all the low-velocity stages during their deceleration, much as if they had entered the target at low velocity. If, then, such a ratio as this is constant for total cathode-ray paths in thick targets, it is constant also for thin targets, and we may state that in any atom struck by a cathode ray of any voltage up to 80 kv., the probability of ionizing a K electron is 0.9 of the probability of emitting a quantum of equivalent energy in the continuous spectrum.

Being dependent on reasoning involving for rigorous formulation the derivative of an experimental result, this law, as applied to the thin target or individual atom, is naturally subject to more relative error than in the thick-target form.

IV. *The Absolute Probability of Direct K Ionization.*—The efficiency of continuous-spectrum excitation is known; therefore, the denominator of the relative probability, Q, can be calculated, and the result can be applied to the determination of the numerator.

Let N_K represent the probability that a cathode ray will ionize a K electron divided for the two processes, direct and indirect, into N'_K and N''_K. Then

$$N'_K = \frac{4\pi PE''}{u_\alpha h\nu_\alpha} e^{+\mu_\alpha \bar{x}} = 2\pi K\nu_K \frac{PE''}{hL} e^{+\mu_\alpha \bar{x}}.$$

K is now calculable from the efficiency of total continuous-spectrum emission, which is

$$MZV = \frac{4\pi}{eV}\int_0^{\nu_0} K(\nu'_0 - \nu)d\nu$$

where M is a constant and Z is the atomic number of silver, 47.

To evaluate this integral, writing $\nu_0(1 + \sigma)$ for ν'_0, it will be assumed, with an error of only a few per cent, that σ is constant at 0.05. Then

$$N'_K = \frac{MZV_K}{1 + 2\sigma} \frac{PE''}{L} e^{+\mu_\alpha \bar{x}}.$$

PE''/L can be found as before, but M is very uncertain. Kulenkampff,[3] by examination of the data at hand in 1926, concluded that M was $(8 \pm 2) \times 10^{-7}$ kv.$^{-1}$; but a later research by Rump,[4] with extreme care, gives efficiency data such as to raise this 8 nearly to 14, about 2 units here being a correction of 20% for loss of cathode rays by reflection, which was not made in former researches but should have been. Under such conditions it is difficult indeed to settle on a value of M to be used and, therefore, in table 3, below, values of N'_K will be listed only in terms of $N'_K/(M \times 10^6$ kv.), with the understanding that $M \times 10^6$ kv. is probably between 1.0 and 1.4.

V. *Thomas' Theory of Direct K Ionization.*—This theory[5] is of especial interest because: (1) it is based on the simple inverse-square law with the conventional circular K orbits and their quantum restrictions; (2) it checks better than any other theory with Wooten's data on intensities of molybdenum Kα-line rays, assuming the arbitrary unit of intensity to be such as to fit the theory at one voltage. The present values of N'_K can be compared with Thomas' formula, without any such arbitrary factor.

Letting N_T stand for Thomas' value of N'_K, his equation may be expressed as

$$N_T = \frac{1}{3S}\left[(s_0 - 1)(2k + 3) - \frac{2k}{k + 1}\log\frac{s_0(2 + k)}{s_0 + 1 + k} - \{3 + (k + 1)(2k + 3)\}\log\frac{s_0 + 1 + k}{2 + k}\right].$$

Here k represents the ratio of the kinetic energy of the K electron to its ionization energy, and S the stopping power of the metal for cathode rays, defined as

$$S = \frac{m^2}{8\pi Ne^4}\left(-\frac{d(v^4)}{dx}\right)$$

N being the number of K electrons per unit volume. For molybdenum, Thomas assumes $k = 1.197$. Assuming it the same for silver, and using Terrill's[6] value of 5.3×10^{43} cm.^{3}/sec.^{4} for $(-d(v^4)/dx)$, the values of N_T to be compared with N'_K are given in table 3.

TABLE 3

v	35	50	65	80 kv.
$N'_K/(M \times 10^6$ kv.)	1.64×10^{-4}	8.55×10^{-4}	1.94×10^{-3}	3.25×10^{-3}
N_T	1.85×10^{-4}	1.00×10^{-3}	2.29×10^{-3}	3.90×10^{-3}
Ratio	1.13	1.17	1.18	1.20

From the last line in this table it is evident that Thomas' theory will agree closely with the values calculated here, if $M = 1.2 \times 10^{-6}$ kv.$^{-1}$, in the middle of the rather wide range of values allowable for it.

VI. *The Nature of the Direct Process of K Ionization.*—The question proposed at the beginning of this paper was, are the directly ionized K electrons usually ejected by the strictly direct process of repulsion by the cathode rays, or more often by the semi-direct, internal photoelectric process? Some evidence on this is now at hand, from two sources.

First, Thomas' theory is based on the hypothesis of strictly direct action, with no mention of the other possibility, and to the previous evidence for it, of fitting the data with an arbitrary factor, is now added the elimination of the arbitrary factor, at least with such limited accuracy as our present knowledge permits.

Second, if the semi-direct process occurred in a large percentage of K ionizations, it would presumably rob the continuous spectrum of some of its energy at frequencies above the K limit and thereby produce a discontinuity in the observed continuous spectrum. The fact that a discontinuity already exists there, because of ordinary absorption associated with indirect K radiation, obscures the evidence. The amount of discontinuity, however, is no more than can readily be accounted for by known laws of cathode-ray penetration, or in fact even less than has often been expected from that cause. Moreover, the K radiation paid for by this discontinuity, assuming it to be indirect, is only $E''-$; if it were semi-direct, it would be something of that order of magnitude. Therefore, it could not in any event give rise to a large fraction of the direct K radiation. Thus, the evidence from this source points to the

same conclusion as that from Thomas' theory, namely, that the direct process is most often strictly direct.

The argument on either line of evidence is not rigorous. The close association between direct ionization and continuous-spectrum emission, shown by the constancy of the relative probability, Q, suggests that the emission of continuous-spectrum quanta by cathode rays must obey laws much like those of the repulsion of other electrons by cathode rays. This idea looks attractive, as perhaps another aspect of similarity between quanta and electrons, and it might lead to an explanation of the behavior of N'_K on an internal photoelectric basis.

Another point where the argument lacks rigor is the assumption that semi-direct ionization would leave its mark on the continuous-emission spectrum. This involves as a basis the assumption that electron jumps between non-periodic states, giving rise to the continuous spectrum, are not encouraged by the prospect of using the energy released for internal photoelectric effect. However, these doubts do not seem to have much evidence behind them, and it seems most probable, in view of all the evidence now at hand, that the direct process of K-electron ionization is most often one of simple repulsion between electrons, obeying laws very much like the ordinary inverse square law.

VII. *Summary.*—1. The assumptions underlying the theory of indirect K ionization, used in the preceding paper and in this one, are tested and found to give results of the right order, though apparently not strictly accurate.

2. The probability of direct K ionization by a cathode ray in silver is found to be 0.9 time the probability of an equivalent quantum emission in the continuous spectrum; this ratio is constant with change of voltage, and, therefore, must hold not only for ordinary, thick targets, but for infinitely thin targets also.

3. The absolute probability of direct K ionization has been estimated, with large limits of error, and the results agree with Thomas' theory.

4. It seems probable that the process of direct ionization is not usually an internal photoelectric effect, but rather a process of repulsion between electrons much like ordinary electrostatic repulsion.

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ANALYSIS OF SPECTRA ARISING FROM QUADRUPLY IONIZED TIN, *Sn V*

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It has been shown[1] for certain sequences of iso-electronic systems that when an electron transition takes place between two levels having the same total quantum number, the resulting lines are displaced to higher and higher frequencies by very nearly a constant value in passing from element

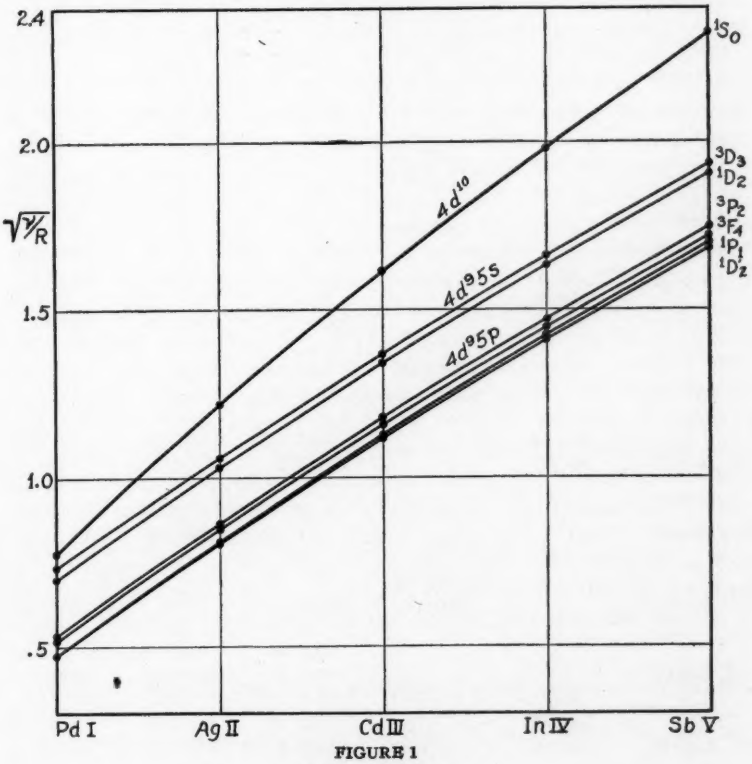

FIGURE 1
Moseley diagram.

to element. Applying this general rule to the spectra of Pd I[2] and Ag II[3], and guided by the Moseley type of diagram for the values of $\sqrt{\nu/R}$ of the terms, by term separations, and by relative intensities, we have been

able to identify most of the strong lines in the spectra of Cd III[4], In IV[4] and Sn V. The spectra reported in this paper were photographed in this laboratory with a new vacuum spectrograph.[4] The lines arising from the transitions $^3PD'F$ and $^1PD'F$ ($4d^95p$) into ^3D and $^1D(4d^95s)$ are

TABLE 1

TIN V

$4d^95p$	$4d^{10}$ $^1S_0$ 0000	$4d^95s$ $^3D_3$ 182586 2478	$^3D_2$ 185064 6142	$^3D_1$ 191206 3025	$^1D_2$ 194231
		15			
		1160.81			
$^3F_4$ 268733		86146.7			
6411		6	12		3
		1254.13	1294.34		1468.64
$^3F_3$ 262322		79736.5	77259.4		68090.2
11013		0	10	4	7
		1101.94	1132.87	1217.60	1264.17
$^3F_2$ 273335		90749.0	88271.3	82128.8	79103.3
		12	4?		4
		1089.40	1119.62		1247.70
$^3D'_3$ 274379		91793.6	89316.2		80147.5
5281			12	10	7
		1155.90?	1189.98	1283.82	1335.70
$^3D'_2$ 269098		86512.4	84035.0	77892.5	74867.0
12067	12		5	8	2
	355.66		1040.57	1111.62	1150.31
$^3D'_1$ 281165	281167		96101.5	89958.8	86933.1
		15			2
		1302.23	1345.64?	.....	1535.00
$^3P_2$ 259377		76791.3	74313.9		65146.5
8620	10		10	3?	6
	373.14		1205.76	1302.23	1355.63
$^3P_1$ 267997	267997		82935.2	76791.3	73766.3
5296				8	
				1218.21	
$^3P_0$ 273293				82087.6	
		4	7		12
		1034.58	1061.80		1176.34
$^1F_3$ 279242		96657.0	94179.6		85009.4
			2	10	10
		.....	1025.09	1093.98	1131.43
$^1D'_2$ 282615			97551.8	91409.4	88383.7
	15		3	3	6
	361.55		1092.58	1171.18	1214.24
$^1P_1$ 276590	276590		91526.4	85384.0	82356.0

found in the region 1000 to 1500 Å. The transitions $^1P_1$, $^3P_1$, and $^3D'_1$-($4d^95p$) into $^1S_0(4d^{10})$, the lowest energy level of the spectrum, were found at 361.55 Å, 373.14 Å and 355.66 Å, respectively, each within one Ångstrom of the wave-length predicted by an extrapolation of the $^1S_0$ and $^1P_1$ lines of

figure 1 from data already known for the first four elements in this sequence.

The intensities, wave-lengths and frequencies of the identified lines are given in table 1 together with the term values referred to $^1S_0(4d^{10})$ as zero. The line $^3D_2 - {}^3D_3'$ as it appears on our plates is much too strong, probably because it is coincident with another line due to some transition in a lower state of ionization. In the case of $^3D_2 - {}^3P_2$, a similar difficulty occurs due to the presence of another strong line from which it is not resolved on our plates. The lines due to transitions $^3D_3 - {}^3P_2$ and $^3D_1 - {}^3P_1$ have the same wave-length thus making it impossible to determine their relative intensities.

Throughout all five of the elements in this sequence the terms arising from $4d^9 5s$ are in the order that would be predicted from Hund's theory. According to Lande's interval rule the $^3D_{1,2,3}$ terms should have the interval ratio 2:3. They are found, however, to be more nearly 2:1. According to Hund's theory $^3F_4$ should be the lowest level arising from the d^9p configuration. Throughout this sequence as well as the corresponding sequence of the first long period[5] $^3P_2$ lies deepest for this configuration. In both sequences the $^3F_3$ term lies deeper than $^3F_4$. Similarly the $^3D_2'$ term lies below the $^3D_3'$ term in this sequence but in the reverse order in the other sequence. The terms $^3F_4$ and $^3P_0$ in these multiplets are each determined by the identification of a single line. In selecting this single line, relative intensities and predicted term separations were taken into consideration. The line $^3D_3 - {}^3F_4$ is, however, one of the strongest lines resulting from these transitions and its location can be predicted with considerable accuracy from a diagram similar to that used in the first long period.[1b,6] The line selected for $^3D_1 - {}^3P_0$ is somewhat less certain but its intensity and the resulting term separations are reasonably satisfactory. Such terms can be fixed with greater certainty when the lines resulting from transitions from $4d^9 5d$ and $4d^9 6s$ to $4d^9 5p$ have been identified. These latter lines are, in general, much weaker and for several of these iso-electronic systems lie in the same region of the spectrum as lines resulting from the transitions from $4d^8 5p$ to $4d^8 5s$ of the once more ionized atoms. We hope soon to extend the analysis here reported for Tin V to Antimony VI.

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1928. (The transitions $4d^9 5p$ to $4d^9 5s$ of Cd III have since been published by McLennan, McLay and Crawford, *Trans. Roy. Soc. Can.*, **22**, III, 1928.) They did not determine the $^1S_0(4d^{10})$ level. The independent identifications made in the two laboratories are in complete agreement. Paper by the authors will appear in the May number of the *Physical Review*.

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ON THE ENERGY AND ENTROPY OF EINSTEIN'S CLOSED UNIVERSE

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1. *Introduction.*—In a preceding article,[1] two principles have been proposed, expressed in a form valid for all sets of coördinates which seem suitable to serve as the analogues in general relativity for the first and second laws of thermodynamics. It is the purpose of the present article to apply these principles to the Einstein closed universe, regarded as filled with a perfect fluid, so as to obtain expressions which may be taken as representing the energy and entropy of this universe. In a following article we shall then use these expressions to investigate the equilibrium between radiation and matter in such a universe, a problem which has recently been attacked in a very stimulating manner by Lenz.[2]

In carrying out our computations, we shall not regard the pressure in the universe as necessarily negligible compared with the energy density, as has hitherto always been done in treatments of the Einstein universe. Our present necessity for abandoning this simplifying assumption arises from the fact that pressure and energy density are necessarily of the same order of magnitude for the case of radiation, and this rules out the simplification in a treatment of the equilibrium between matter and radiation. Owing to this fact that we do not neglect the pressure, the expression that we obtain for the energy of the universe will differ from that previously obtained by Einstein[3] with the use of the simplifying assumption. Our expression for energy also differs from that tacitly taken by Lenz for his treatment of the equilibrium between radiation and matter, but our expression for the entropy turns out to be the same as that which he assumed.

2. *Metrical Properties of the Einstein Universe.*—Before we can apply the laws of thermodynamics to the Einstein universe, we must consider

its metrical properties. These are contained in the form assumed for the line element

$$ds^2 = -R^2 d\chi^2 - R^2 \sin^2 \chi (d\theta^2 + \sin^2 \theta d\phi^2) + dt^2 \quad (1)$$

giving us

$$g_{11} = -R^2, \quad g_{22} = -R^2 \sin^2 \chi, \quad g_{33} = -R^2 \sin^2 \chi \sin^2 \theta, \quad g_{44} = 1 \quad (2)$$
$$g^{\mu\nu} = 1/g_{\mu\nu} \ (\mu = \nu), \qquad g^{\mu\nu} = g_{\mu\nu} = 0 \quad (\mu \neq \nu)$$

and

$$\sqrt{-g} = R^3 \sin^2 \chi \sin \theta. \quad (3)$$

Furthermore, these values of the fundamental tensor $g_{\mu\nu}$ lead, as is well known,[4] to the following components of the contracted Riemann-Christoffel tensor

$$G_{11} = -2, \quad G_{22} = -2 \sin^2 \chi, \quad G_{33} = -2 \sin^2 \chi \sin^2 \theta, \quad G_{44} = 0 \quad (4)$$

and for the invariant spur of this tensor

$$G = 6/R^2. \quad (5)$$

3. *Relation between Metrical Properties and Energy Tensor.*—The above metrical properties will be related to the energy tensor $T_{\mu\nu}$ for matter and electricity by the fundamental equation[5]

$$-8\pi T_{\mu\nu} = G_{\mu\nu} - \tfrac{1}{2} g_{\mu\nu} G + \lambda g_{\mu\nu} \quad (6)$$

where the factor 8π simplifies the coördination of units and λ is a constant small enough so that the last term can be neglected except in the consideration of very large systems such as the whole universe. The justification for this equation is given by the consideration that the divergence of the left-hand side vanishes because of the physical facts concerning the behavior of energy and momentum, and the divergence of the right-hand side vanishes identically. Hence, if we desire a geometrical interpretation of energy and momentum the identification of the two sides of (6) appears natural.

To obtain an expression for the energy tensor $T_{\mu\nu}$ we shall assume the substance filling the universe to be a uniformly distributed perfect fluid, since we shall later wish to consider it as a mixture of perfect gas and radiation. For such a fluid it is well known that the energy tensor assumes the form[6]

$$T^{\mu\nu} = (\rho_{00} + p) \frac{dx_\mu}{ds} \frac{dx_\nu}{ds} - g^{\mu\nu} p \quad (7)$$

where ρ_{00} is the *proper macroscopic* density of the fluid, p its *proper* pressure

and $d\chi_\mu/ds$ refers to its *macroscopic* motion. Since the fluid is taken as macroscopically stationary in the coördinates chosen, we have

$$\frac{d\chi}{ds} = \frac{d\theta}{ds} = \frac{d\phi}{ds} = 0, \qquad \frac{dt}{ds} = 1 \tag{8}$$

and the energy tensor reduces to the terms in its leading diagonal

$$T^{11} = -g^{11}p, \quad T^{22} = -g^{22}p, \quad T^{33} = -g^{33}p, \quad T^{44} = \rho_{00} \tag{9}$$

or lowering suffixes

$$T^1_1 = -p, \quad T^2_2 = -p, \quad T^3_3 = -p, \quad T^4_4 = \rho_{00} \tag{10}$$

and lowering suffixes again

$$T^{11} = -g_{11}p \quad T_{22} = -g_{22}p \quad T_{33} = -g_{33}p \quad T_{44} = \rho_{00}. \tag{11}$$

By substituting equations (2), (4), (5) and (11) into (6) we now easily obtain the desired relations between the material properties of the universe as given in terms of ρ_{00} and p and the metrical properties as given in terms of R and λ,

$$8\pi p = -\frac{1}{R^2} + \lambda \tag{12}$$

$$8\pi\rho_{00} = \frac{3}{R^2} - \lambda \tag{13}$$

$$\rho_{00} + p = \frac{1}{4\pi R^2}. \tag{14}$$

4. *Application of the First Law.*—We are now ready to apply the first law of thermodynamics as given in the previous article (l. c.) by the equation

$$\int\int\int\int \left(\frac{\partial \mathfrak{T}^\nu_\mu}{\partial x_\nu} - \frac{1}{2}\mathfrak{T}^{\alpha\beta}\frac{\partial g_{\alpha\beta}}{\partial x_\mu} \right) dx_1 dx_2 dx_3 dx_4 = 0 \tag{15}$$

where the integration is to be taken over the total spatial volume of the universe and over any desired time interval. Equation (15) is not a tensor equation since the integration is taken over a finite region, nevertheless as pointed out in the previous article the equation is true in all sets of coördinates since the integrand is itself equal to zero in all sets of coördinates at all points in space-time.

To use equation (15) for our present purposes it is desirable to transform the integrand into the form of an ordinary divergence by re-expressing the second term in the integrand in terms of Einstein's pseudo-tensor of gravitational energy. We obtain

$$\int\int\int\int \frac{\partial(\mathfrak{T}^\nu_\mu + \mathfrak{t}^\nu_\mu)}{\partial x_\nu} dx_1 dx_2 dx_3 dx_4 = 0 \tag{16}$$

where the pseudo-tensor t_μ^ν is known[7] to have the following value in terms of the fundamental tensor and its derivatives,

$$t_\mu^\nu = \frac{1}{16\pi}\left(g_\mu^\nu \mathfrak{L} - \mathfrak{g}_\mu^{\alpha\beta}\frac{\partial \mathfrak{L}}{\partial \mathfrak{g}_\nu^{\alpha\beta}}\right) + \frac{1}{8\pi} g_\mu^\nu \lambda \sqrt{-g} \tag{17}$$

with

$$\left.\begin{aligned} \mathfrak{L} &= g^{\rho\sigma}\sqrt{-g}\,[\{\rho\alpha,\beta\}\{\sigma\beta,\alpha\} - \{\rho\sigma,\alpha\}\{\alpha\beta,\beta\}] \\ \mathfrak{g}_\mu^{\alpha\beta} &= \frac{\partial}{\partial x_\mu}(g^{\alpha\beta}\sqrt{-g}) \end{aligned}\right\} \tag{18}$$

and

$$\frac{\partial \mathfrak{L}}{\partial \mathfrak{g}_\nu^{\alpha\beta}} = g_\alpha^\nu\{\beta\rho,\rho\} - \{\alpha\beta,\nu\}.$$

The calculation of the pseudo-tensor with the help of these equations is very lengthy. Nevertheless, evaluating the Christoffel three index symbols in terms of the fundamental tensor as given by equations (2), and substituting in (18) and (17), we finally obtain in agreement with Einstein (l. c.)

$$\left.\begin{aligned} &8\pi t_1^1 = R\cos^2\chi\sin\theta + \lambda\sqrt{-g}, \quad 8\pi t_2^1 = R\sin\chi\cos\chi\cos\theta \\ &8\pi t_2^2 = 8\pi t_3^3 = 8\pi t_4^4 = -R\cos^2 x\sin\theta + \lambda\sqrt{-g} \end{aligned}\right\} \tag{19}$$

the values with all other combinations of the indices being zero.

We are now ready to apply equation (16). We shall be interested for thermodynamic purposes in the case $\mu = 4$ which gives information as to energy relationships, cases $\mu = 1$, 2 and 3 giving information as to momenta. Referring to equations (10) and (19), we note that $(\mathfrak{T}_4^\nu + t_4^\nu)$ and $\partial(\mathfrak{T}_4^\nu + t_4^\nu)/\partial\chi_\nu$ are equal to zero for all values of ν except $\nu = 4$ and our principle as given by equation (16) reduces to

$$\int_t^{t'}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\frac{\partial}{\partial t}\left(\rho_{00}\sqrt{-g} - \frac{R}{8\pi}\cos^2\chi\sin\theta + \frac{\lambda}{8\pi}\sqrt{-g}\right)d\chi d\theta d\phi dt = 0. \tag{20}$$

And substituting the values of λ and $\sqrt{-g}$ given by equations (12) and (3) this can be rewritten in the form

$$\int_t^{t'}\frac{d}{dt}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\left\{(\rho_{00}+p)\sqrt{-g} - \frac{R}{8\pi}\cos^2\chi\sin\theta + \frac{R}{8\pi}\sin^2\chi\sin\theta\right\}d\chi d\theta d\phi dt = 0. \tag{21}$$

On integration with respect to χ we find, however, that the last two terms

contribute nothing to the expression, and we obtain the simple result

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} (\rho_{00} + p)\sqrt{-g}\, d\chi d\theta d\phi = \text{const.} \qquad (22)$$

where the constant is independent of the time.

Furthermore, in our coördinates in accordance with equations (8), t is the *proper* time so that we can write

$$d\chi = \sqrt{-g}\, d\chi d\theta d\phi dt = dV dt$$

and

$$V = \int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} \sqrt{-g}\, d\chi d\theta d\phi = 2\pi^2 R^3 \qquad (23)$$

where dV is the element of *proper spatial* volume occupied by the material in the universe. Hence, equation (22) can also be written in the form

$$(\rho_{00} + p)V = \text{const.} \qquad (24)$$

where V is the total spatial volume of the universe.

We may regard this quantity $(\rho_{00} + p)V$, whose value doesn't change with the time, as an expression for the energy of the universe. It differs from the quantity $\rho_0 V$ obtained by Einstein (l. c.), since we have taken the pressure into account, and also differs from the value assumed by Lenz, who used an expression which in our nomenclature would be $\rho_{00}V$.

5. *Application of the Second Law.*—We must now consider the application of the second law of thermodynamics as given in the previous article (l. c.) by the equation

$$\int\int\int\int \frac{\partial \mathfrak{S}^{\mu}}{\partial x_{\mu}}\, dx_1 dx_2 dx_3 dx_4 \geqq 0. \qquad (25)$$

For the entropy vector we have the equation of definition given in the previous article

$$S^{\mu} = \phi_0 \frac{dx_{\mu}}{ds} \qquad (26)$$

where ϕ_0 is the proper density of entropy and dx_{μ}/ds refers to the macroscopic motion of the matter in the universe. Referring to equations (8), we see that the entropy vector reduces to a very simple form and equation (25) becomes

$$\int_t^{t'}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} \frac{\partial}{\partial t}(\phi_0\sqrt{-g}) d\chi d\theta d\phi dt \geqq 0 \qquad (27)$$

which in accordance with equation (23) can be rewritten in the form

$$(\phi_0 V)_{t'} - (\phi_0 V)_t \geqq 0. \qquad (28)$$

Hence $\phi_0 V$ is a quantity which can only increase with the time and may be regarded as the entropy of the universe. This quantity proves to be equivalent to the expression that Lenz took for the entropy of the Einstein universe, but, in general, the expression for the entropy of a system in a gravitational field does not reduce to so simple a form.

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[3] Einstein, A., *Berl. Ber.*, 448–459 (1918).

[4] See Eddington, A. S., *The Mathematical Theory of Relativity*, Cambridge, 1923, equations (69.21) and (69.22).

[5] See Eddington, l. c., equation (54.71).

[6] See Eddington, l. c., equations (54.81) and (54.82).

[7] See Eddington, equations (59.4), (58.1), (58.45) and (58.52). The additional term in λ can easily be shown necessary where the full form of equation (6) is used. Compare Einstein, l. c.

ON THE EQUILIBRIUM BETWEEN RADIATION AND MATTER IN EINSTEIN'S CLOSED UNIVERSE

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1. *Introduction.*—In two preceding articles,[1] the principles of thermodynamics have been expressed in a form suitable for applications in general relativity, and then applied to Einstein's closed universe, employing a set of coördinates in which the line element assumes the form

$$ds^2 = -R^2 d\chi^2 - R^2 \sin^2 \chi (d\theta^2 + \sin^2 \theta d\phi^2) + dt^2. \qquad (1)$$

Using these coördinates, and assuming the universe filled with a perfect fluid whose pressure is not necessarily negligible, the general relativity analogue of the first law of thermodynamics was found to lead to the equation

$$(\rho_{00} + p)V = \text{const.} \qquad (2)$$

where ρ_{00} is the *proper macroscopic* density and p the *proper* pressure of the fluid. And the analogue of the second law of thermodynamics was found to lead to the expression

$$(\phi_0 V)_{t'} - (\phi_0 V)_t \geqq 0 \qquad (3)$$

where ϕ_0 is the *proper* density of entropy of the fluid, and $\phi_0 V$ is found, as indicated, to be a quantity which can only increase with the time.

In both of these expressions V is the *proper* volume of the material in the universe as given by the expression

$$V = \int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} R^3 \sin^2\chi \sin\theta d\chi d\theta d\phi = 2\pi^2 R^3. \tag{4}$$

Furthermore, the metrical and material properties of the universe were found to be related by the equation

$$\rho_{00} + p = \frac{1}{4\pi R^2} \tag{5}$$

which combined with equation (4) gives us

$$V = \frac{\pi^{1/2}}{4(\rho_{00} + p)^{3/2}}. \tag{6}$$

2. *Conditions of Equilibrium.*—We are now ready to consider the condition of thermodynamic equilibrium in such a universe. In accordance with equations (2) and (3), this will evidently be attained when we have the maximum possible value of $\phi_0 V$, compatible with a constant value of $(\rho_{00} + p)V$. Substituting the value of V given by equation (6), we easily find that this leads to the equations

$$\delta\phi_0 = 0 \tag{7}$$

and

$$\delta(\rho_{00} + p) = 0 \tag{8}$$

as the condition of equilibrium.

3. *Consideration of the Fluid as a Mixture of a Perfect Gas and Radiation.*—If now we consider that the fluid filling the universe is a mixture of a perfect gas and radiation, we can evidently write[2]

$$\phi_0 = Nk \log \frac{bT^{3/2}}{N} + \frac{5}{2} Nk + \frac{4}{3} aT^3 \tag{9}$$

and

$$\rho_{00} + p = Nmc^2 + \frac{5}{2} NkT + \frac{4}{3} aT^4 \tag{10}$$

where N is the number of molecules of gas per unit volume, k is Boltzmann's constant, b a constant which assures the same starting point for the entropy of gas and radiation,[2] T is the absolute temperature, a is Stefan's constant, m is the mass of one molecule and c is the velocity of light.

These expressions are functions of the concentration N and temperature T, and by performing the variations indicated by equations (7) and (8) with respect to these quantities, we have

$$\left(k \log \frac{bT^{3/2}}{N} - k + \frac{5}{2}k\right)\delta N + \left(\frac{3}{2}\frac{Nk}{T} + 4aT^2\right)\delta T = 0 \quad (11)$$

and

$$\left(mc^2 + \frac{5}{2}kT\right)\delta N + \left(\frac{5}{2}Nk + \frac{16}{3}aT^3\right)\delta T = 0. \quad (12)$$

Combining and rearranging, we can then solve for N in the form

$$N = bT^{3/2}\, e^{-\alpha\frac{mc^2}{kT} - \frac{5}{2}\alpha + \frac{3}{2}} \quad (13)$$

where α has the value

$$\alpha = \frac{3/2\, Nk + 4aT^3}{5/2\, Nk + 16/3aT^3} \quad (14)$$

and hence lies within the narrow limits

$$\frac{3}{5} < \alpha < \frac{3}{4}. \quad (15)$$

5. *Conclusion.*—The above result for the equilibrium concentration of a perfect gas in the Einstein closed universe may be compared with the results obtained by Stern[3] and by the present writer[4] from thermodynamic considerations which in both cases tacitly assumed *flat space-time.* The writer's result was

$$N = bT^{3/2}\, e^{-\frac{mc^2}{kT}} \quad (16)$$

and the earlier result of Stern, which led to a definite although not necessarily correct value of the constant b, was

$$N = \left(\frac{2\pi mk}{h^2}\right)^{3/2} T^{3/2}\, e^{-\frac{mc^2}{kT}}. \quad (17)$$

Comparing equations (13), (16) and (17), and noting the limits to the possible values of α, we see that the original result of Stern and the writer, valid in flat space-time, is not greatly altered by the gravitational field in the closed universe which we have here considered. At all reasonable temperatures the concentration of molecules, even of mass as small as the electron, would still come out exceedingly small on account of the great effect of the exponential term $-mc^2/kT$, unless the constant b could be shown to have an enormous value.

This conclusion is very different from the result reached by Lenz[5] in his treatment of the equilibrium between radiation and matter in Einstein's closed universe, since he obtained even at low temperatures an approximate equality between the densities of energy in the form of gas and radiation,

instead of a practical disappearance of matter. The treatment of Lenz differed from the present one in that he based it on assumed expressions for the energy and volume of the Einstein universe quite different from those that we have obtained as the natural result of our method of development. In particular, his assumption that the volume of the universe is increased by the presence of matter, but unaffected by the presence of radiation, had a great effect in favoring the production of matter. It would be of considerable interest if some logical justification could be found for such an assumption.

[1] Tolman, R. C., these PROCEEDINGS, **14**, No.3, 268–272; No.4, 348–353 (1928).

[2] If we take the entropy of a crystal as zero at the absolute zero of temperature, the entropy density of a perfect monatomic gas formed from it by vaporization is given by the Sackur-Tetrode equation

$$\phi_0 = Nk \log \left(\frac{2\pi mk}{h^2}\right)^{3/2} \frac{T^{3/2}}{N} + \frac{5}{2} Nk$$

since, however, the change in entropy in forming the crystal from radiation is unknown we must add a term Nk log (const.), to assure the same starting point as for the entropy-density expression, $4/3\ aT^3$ for radiation. This term with certain other constant factors is included in the Nk log b occurring in our expression.

[3] Stern, O., *Z. Electrochem.*, **31**, 448–449 (1925); *Trans. Farad. Soc.*, **21**, 477–478 (1925–6).

[4] Tolman, R. C., these PROCEEDINGS, **12**, 670–674 (1926).

[5] Lenz, W., *Physik. Z.*, **27**, 642–645 (1926).

PHOTOCHEMICAL OZONIZATION AND ITS RELATION TO THE POLYMERIZATION OF OXYGEN

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In an article which has been presented to the *Journal of the American Chemical Society* for publication the author has shown that the results of experiments on photochemical ozonization and on the absorption of light by oxygen afford important evidence for the existence of a polymer of the molecule O_2 in oxygen gas.

The quantitative researches of Warburg[1] have demonstrated that in oxygen gas at high pressures ozone is formed at wave-lengths 2090 Å and 2530 Å. Recent spectroscopic results[2] show, however, that the molecule O_2 does not absorb in this region. The absorption of oxygen at these wave-lengths, resulting in ozonization, is evidence that there exists in oxygen another molecular form of this element than the molecule O_2.

Furthermore, Warburg found that the conditions of ozonization at

wave-length 2090 Å (in contrast to those at 2530 Å) nearly satisfied the photochemical equivalence equation. In an endothermic reaction this presumably shows that the primary act is dissociation of the molecule as Warburg assumed, for although there appeared for a time to be theoretical reasons against this, these are no longer sufficient, and as an empirical fact this assumption appears to be true. But the most probable value for the heat of dissociation of the molecule O_2 is equivalent to 7 volts,[2] dissociation taking place by light absorption first at about 1765 Å. The above-mentioned wave-length used by Warburg is far to the red of this. Thus it appears probable that there exists in oxygen gas another molecule than O_2, for which the absorption of wave-length 2090 Å, leads directly to dissociation.

Professor G. N. Lewis[3] has given evidence that there is polymerization in oxygen and, in particular, from the data on the magnetic susceptibility of oxygen at low temperatures, has computed a value for the change in heat content accompanying this polymerization. He concludes that at the temperature of liquid air, or at room temperature and very high pressures, an appreciable fraction of the oxygen is in the form of the molecule O_4. Experiments on the absorption of light by oxygen at high pressures support this, and indicate that the polymer is the molecule O_4. Bands appear in the visible and ultra-violet which are of a different character than the bands due to O_2. Also they increase in intensity not as the pressure, but more nearly as the square of the pressure. Furthermore, a region of complete absorption begins in the ultra-violet, and this appears to be preceded by discontinuous absorption. This is characteristic of dissociation by the absorption of light. An extrapolation of the semi-quantitative data given by Liveing and Dewar[4] on the limit of transparency at three different pressures places the beginning of the continuous absorption in the vicinity of the position, where it might be expected to begin if it represents the dissociation of the molecule O_4 into ozone molecule and oxygen atom. This position may be computed to be approximately 2470 Å, since the energy changes in the dissociation of O_4 molecule giving two O_2 molecules, in the dissociation of O_2 and in the formation of O_3 are known. These points are evidence that the molecule O_4 is responsible for this new absorption in oxygen and, in addition, give a plausible explanation of the result of Warburg's photochemical experiments. As discussed above, these indicate a dissociation process for the absorption of wave-length 2090 Å, but do not for 2530 Å, and it appears that only the former lies in the continuous spectrum.

Warburg[5] has measured the absorption for wave-lengths 2090 Å and 2530 Å through a range of pressures reaching nearly to 400 atmospheres, and for the first wave-length, in both 95% oxygen and in air. Qualitatively the character of the change of the absorption with the pressure

agrees well with the opinion that the absorption is due to the molecule O_4. Thus it increases somewhat less rapidly than as the square of the total pressure, especially at the high pressures. The equilibrium involved may be expressed by the equation

$$K_p = \frac{p_{O_2}^2}{p_{O_4}} = \frac{(P - p_{O_4})^2}{p_{O_4}}$$

P being the total pressure. It is clear that for pressures at which p_{O_4} is no longer negligible compared with P, the proportionality to the square of the pressure will no longer hold, and at very high pressures the absorption will approach proportionality to the pressure. A marked difference was found in the absorption of the oxygen in air and that in 95% oxygen, it being greater in the former than in the latter. This does not, however, contradict the belief that the absorption is due to the O_4 molecule, since the equilibrium expressed above is probably considerably altered in the presence of a large concentration of foreign molecules.

From Warburg's data it is possible to make quantitative estimation of the equilibrium constant K_p. The value so found is 549 kgm./cm.^{2} We may express this in other units as $K_\rho = 0.35$ gm./cm.^{3} Professor Lewis, in his treatment of the magnetic measurements of Perrier and Onnes, obtained, for room temperature, the value $K_\rho = 4$ gm./cm.^{3} That the same order of magnitude is obtained by two quite independent methods is significant and the agreement satisfactory when it is considered that the calculations were made at widely different temperatures, and that assumptions which could only be approximately true were made in this treatment of the absorption data.

The hypothesis has been held that this new absorption, which appears in oxygen at high pressures, is due to the influence of molecular impacts on the absorption of the molecule O_2. There are several reasons why this seems no longer tenable. These concern the position of the absorption, its behavior as the pressure and temperature are varied, and the characteristics of the ultra-violet absorption of oxygen. Finally, Liveing and Dewar in their observations always observed the first two of the atmospheric bands of oxygen as well as the new absorption. They comment on the fact that the lines of the former bands at these pressures appeared much broader than in the ordinary solar spectrum. Thus this affords at once an example of the influence of pressure on molecular absorption, and at the same time, evidence that such an effect is small, of a different order of magnitude than the phenomenon of the new absorption at these pressures.

This work had its origin in discussion with Professor T. R. Hogness of this Laboratory, and the author gladly acknowledges his indebtedness to him for valuable suggestions.

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[1] Warburg, *Berl. Ber.*, p. 746, **1911**; p. 216, **1912**; p. 872, **1914**; *Z. Elektrochem.* **26**, 54 (1920); **27**, 133 (1921).

[2] Birge and Sponer, *Physic. Rev.*, **28**, 259–283 (1926).

[3] Lewis, *J. Amer. Chem. Soc.*, **46**, 2027–2032 (1924).

[4] Liveing and Dewar, *Proc. Roy. Soc.*, **46**, 222 (1889).

[5] Warburg, *Berl. Ber.*, p. 230, **1915**.

THE SHARED-ELECTRON CHEMICAL BOND

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With the development of the quantum mechanics it has become evident that the factors mainly responsible for chemical valence are the Pauli exclusion principle and the Heisenberg-Dirac resonance phenomenon. It has been shown[1,2] that in the case of two hydrogen atoms in the normal state brought near each other the eigenfunction which is symmetric in the positional coördinates of the two electrons corresponds to a potential which causes the two atoms to combine to form a molecule. This potential is due mainly to a resonance effect which may be interpreted as involving an interchange in position of the two electrons forming the bond, so that each electron is partially associated with one nucleus and partially with the other. The so-calculated heat of dissociation, moment of inertia, and oscillational frequency[2] of the hydrogen molecule are in approximate agreement with experiment. London[3] has recently suggested that the interchange energy of two electrons, one belonging to each of two atoms, is the energy of the non-polar bond in general. He has shown that an antisymmetric (and hence allowed) eigenfunction symmetric in the coordinates of two electrons can occur only if originally the spin of each electron were not paired with that of another electron in the same atom. The number of electrons with such unpaired spins in an atom is, in the case of Russell-Saunders coupling, equal to $2s$, where s is the resultant spin quantum number, and is closely connected with the multiplicity, $2s + 1$, of the spectral term. This is also the number of electrons capable of forming non-polar bonds. The spins of the two electrons forming the bond become paired, so that usually these electrons cannot be effective in forming further bonds.

It may be pointed out that this theory is in simple cases entirely equivalent to G. N. Lewis's successful theory of the shared electron pair, advanced in 1916 on the basis of purely chemical evidence. Lewis's electron

pair consists now of two electrons which are in identical states except that their spins are opposed. If we define the chemical valence of an atom as the sum of its polar valence and the number of its shared electron pairs, the new theory shows that the valence must be always even for elements in the even columns of the periodic system and odd for those in the odd columns. The shared electron structures assigned by Lewis to molecules such as H_2, F_2, Cl_2, CH_4, etc., are also found for them by London. The quantum mechanics explanation of valence is, moreover, more detailed and correspondingly more powerful than the old picture. For example, it leads to the result that the number of shared bonds possible for an atom of the first row is not greater than four, and for hydrogen not greater than one; for, neglecting spin, there are only four quantum states in the L-shell and one in the K-shell.

A number of new results have been obtained in extending and refining London's simple theory, taking into consideration quantitative spectral and thermochemical data. Some of these results are described in the following paragraphs.

It has been found that a sensitive test to determine whether a compound is polar or non-polar is this: If the internuclear equilibrium distance calculated for a polar structure with the aid of the known properties of ions agrees with the value found from experiment, the molecule is polar; the equilibrium distance for a shared electron bond would, on the other hand, be smaller than that calculated. Calculated[4] and observed values of the hydrogen-halogen distances in the hydrogen halides are in agreement only for HF, from which it can be concluded that HF is a polar compound formed from H^+ and F^- and that, as London had previously stated, HCl, HBr, and HI are probably non-polar. This conclusion regarding HF is further supported by the existence of the hydrogen bond. The structure $\left[:\ddot{F}:H:\ddot{F}:\right]^-$ for the acid fluoride ion and a similar one for H_6F_6 are ruled out by Pauli's principle, if the shared pairs be of London's type. The ionic structure $:\ddot{F}:^- H^+ :\ddot{F}:^-$, in which the proton holds the two fluoride ions together by electrostatic forces (including polarization), is, of course, allowed. This conception of the hydrogen bond, requiring the presence of a proton, explains the observation that only atoms of high electron affinity (fluorine, oxygen, and nitrogen) form such bonds.

Compounds of septivalent chlorine probably contain chlorine with a polar valence of +3 and with four shared electron bonds. Thus the perchlorate ion would be formed from $\cdot\dot{C}l\cdot^{+3}$ and $4\cdot\ddot{O}:^-$ and would have the structure $\left[\begin{array}{c} :\ddot{O}: \\ :\ddot{O}:\ddot{Cl}:\ddot{O}: \\ :\ddot{O}: \end{array}\right]^-$. This structure is, of course, also possible

for FO_4^-, inasmuch as there are positions for four (and only four) unpaired electrons in the L-shell of fluorine. London assumed that septivalent chlorine had a polar valence of zero and seven shared electron bonds, and pointed out in explanation of the non-existence of valences other than one for fluorine that seven unpaired L-electrons cannot occur. This simple explanation, however, does not make impossible fluorine with a polar valence of +3 and with four shared bonds; the non-existence of higher valences of fluorine must accordingly instead be explained on energetic considerations, and is connected with its very large ionization potentials.

In the case of some elements of the first row the interchange energy resulting from the formation of shared electron bonds is large enough to change the quantization, destroying the two sub-shells with $l = 0$ and $l = 1$ of the L-shell. Whether this will or will not occur depends largely on the separation of the s-level ($l = 0$) and the p-level ($l = 1$) of the atom under consideration; this separation is very much smaller for boron, carbon, and nitrogen than for oxygen and fluorine or their ions, and as a result the quantization can be changed for the first three elements but not for the other two. The changed quantization makes possible the very stable shared electron bonds of the saturated carbon compounds and the relatively stable double bonds of carbon, which are very rare in other atoms, and in particular are not formed by oxygen. This rupture of the l-quantization also stabilizes structures in which only three electron pairs are attached to one atom, as in molecules containing a triple bond ($N_2 = \dot{N}:::\dot{N}$), the carbonate, nitrate, and borate ions $\left(\left[:\ddot{O}:C\begin{matrix}\dot{O}\\ \dot{O}\end{matrix}\right]^-\right)$, etc.), the carboxyl group, $R:C\begin{matrix}\dot{O}\\ \dot{O}:H\end{matrix}$, and similar compounds. It has further been found that as a result of the resonance phenomenon a tetrahedral arrangement of the four bonds of the quadrivalent carbon atom is the stable one.

Electron interactions more complicated than those considered by London also result from the quantum mechanics, and in some cases provide explanations for previously anomalous molecular structures.

It is to be especially emphasized that problems relating to choice among various alternative structures are usually not solved directly by the application of the rules resulting from the quantum mechanics; nevertheless, the interpretation of valence in terms of quantities derived from the consideration of simpler phenomena and susceptible to accurate mathematical investigation by known methods now makes it possible to attack them with a fair assurance of success in many cases.

The detailed account of the material mentioned in this note will be submitted for publication to the *Journal of the American Chemical Society*.

[1] Heitler, W., and London, F., *Z. Phys.*, **44**, 455 (1927).

[2] Y. Sugiura, *Ibid.*, **45**, 484 (1927).

[3] F. London, *Ibid.*, **46**, 455 (1928).

[4] L. Pauling, *Proc. Roy. Soc.*, **A114**, 181 (1927). In this paper it was stated that the consideration of polarization of the anion by the cation would be expected to reduce the calculated values; a number of facts, however, indicate that with ions with the noble gas structure the effect of polarization on the equilibrium distance is small.